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*Canadian Environmental Protection Act, 1999*

# PRIORITY SUBSTANCES LIST

# ASSESSMENT REPORT

# ROAD SALTS

Environment Canada
Health Canada

August 2000

101-01993/

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## LIST OF ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| CAS | Chemical Abstracts Service |
| CEPA | *Canadian Environmental Protection Act* |
| CEPA 1999 | *Canadian Environmental Protection Act, 1999* |
| CI | confidence interval |
| CTV | Critical Toxicity Value |
| EC | Electrical Conductivity |
| $EC_{50}$ | median effective concentration |
| EEV | Estimated Exposure Value |
| ENEV | Estimated No-Effects Value |
| ESA | environmental site assessment |
| ESR | Exchangeable Sodium Ratio |
| GTA | Greater Toronto Area |
| $IC_{50}$ | median inhibitory concentration |
| $K_{oc}$ | organic carbon/water partition coefficient |
| $K_{om}$ | soil sorption coefficient |
| $K_{ow}$ | octanol/water partition coefficient |
| kg-bw | kilogram body weight |
| $LC_{50}$ | median lethal concentration |
| $LD_{50}$ | median lethal dose |
| LOAEC | Lowest-Observed-Adverse-Effect Concentration |
| LOAEL | Lowest-Observed-Adverse-Effect Level |
| LOEC | Lowest-Observed-Effect Concentration |
| LOEL | Lowest-Observed-Effect Level |
| LOF | land occupation factor |
| MTO | Ministry of Transportation of Ontario |
| MTQ | Ministry of Transportation of Quebec |
| NOAEL | No-Observed-Adverse-Effect Level |
| NOEC | No-Observed-Effect Concentration |
| NOEL | No-Observed-Effect Level |
| OP | Osmotic Potential |
| PSL | Priority Substances List |
| TDS | total dissolved salt |

## SYNOPSIS

Road salts enter the Canadian environment through their storage and use and through disposal of waste snow. Road salts are used for de-icing and anti-icing winter road maintenance, with some use as summer dust suppressants. Inorganic chloride salts considered in this assessment include sodium chloride, calcium chloride, potassium chloride and magnesium chloride; in the environment, these dissociate into the chloride anion and the corresponding cation. In addition, ferrocyanide salts, which are added as anti-caking agents in road salts formulations, were assessed. It is estimated that approximately 4 750 000 tonnes of sodium chloride de-icers were used in the 1997–98 winter and that 110 000 tonnes of calcium chloride are used on roadways in a typical year. When combined, it is estimated that 2 950 000 tonnes of chloride were released to the environment in Canada in the 1997–98 winter season. Very small amounts of other salts were used.

These compounds enter surface water, soil and groundwater after snowmelts, and are dispersed by splash and spray through the air. Chloride ions are conservative which means that the ion follows water without being retarded or lost from flowing water. All chloride ions that enter groundwater can ultimately be expected to reach surface water; it may take from a few years to several decades or more for steady-state groundwater concentrations to be reached.

Because of the widespread dispersal through the environment, environmental concerns can be associated with most environmental compartments. In water, natural background concentrations of salts can be high in some areas of the Prairies and British Columbia. In other regions, concentrations in water are in the order of a few mg/L. High concentrations of chloride related to use of road salts on roadways have been measured in water, for example with reported maxima of about 19 000 mg/L in road runoff, 89 000 mg/L in meltwater, 13 500 mg/L in wetlands, 8500 mg/L in ditches and streams, 4310 mg/L in small rivers and 150 mg/L in rural lakes and 2000 to 3000 mg/L in urban impoundment lakes. In groundwater, concentrations as high as 2800 mg/L have been associated with storage yards with concentrations of about 400 mg/L being associated with general area-wide urban inputs. Modelling and field measurements have indicated key concerns in urban areas of high use, notably in southern Ontario, Quebec and the Maritimes. Field measurements have shown that roadway applications in rural areas can also result in increased concentrations of chloride even in lakes a few hundred meters away from roadways.

Toxic effects to aquatic biota have been associated in the laboratory with exposures to chloride concentrations as low as 400 mg/L for non-lethal effects (fungi) and 874 989 and 1068 mg/L for median lethal effects (fathead minnow embryos, rainbow trout egg/embryos, daphnids, respectively). The No-Observed-Effect Concentration (NOEC) for the 33-day early stage test for survival of fathead minnow was 252 mg/L chloride, with a Lowest-Observed-Effect Concentration (LOEC) (9% reduction in survivorship) of 352 mg/L. Modelling using acute to chronic ratios indicates possible median lethal effects at concentrations as low as 210 mg/L

chlorides for daphnids. About 5% of aquatic species would be affected (median lethal concentration) at chloride concentrations of about 210 mg/L, while 10% of species would be affected at chloride concentrations of about 240 mg/L. Changes in populations or community structure can occur at lower concentrations. Because of differences in optimal chloride concentrations for different species of algae, shifts in populations in lakes were associated with concentrations of 12 to 235 mg/L. High concentrations of chloride in lakes can also increase availability of metals and, by preventing seasonal mixing of waters, affect distribution of oxygen and nutrients.

In soils, a limited number of measurements are available which correlate soil concentrations with biological effects or with direct abiotic effects on soils. Modelling studies of the salt concentrations in soil from roadways was done and indicated that impacts should be limited to areas in or close to the rights of way. Studies also indicated that sensitive microorganisms may be affected by soil concentrations of about 60 ppm Na and 90 ppm Cl and above. Soil concentrations exceeding these levels have been reported within about 30 m from the edges of highways in Canada and have also been reported for soils at patrol yards.

Laboratory and field data have correlated damage to vegetation with distance from treated roadways and concentrations of sodium and chloride in plant tissues. Sensitive terrestrial plants may be affected by soil concentrations of about 68 ppm Na and 215 ppm Cl and above, or by tissue concentrations of about 575 ppm Na and 800 ppm Cl and above. Concentrations exceeding these soil levels have been reported within about 30 m from the edges of highways in Canada and in patrol yards, and concentrations exceeding these tissue concentrations have been reported within about 100 m from the edges of Canadian highways. A number of field studies have documented damage to vegetation and shifts in plant community structure near roadways resulting from the use of road salts.

Behavioural and toxicological impacts have been associated with exposure of mammalian and avian wildlife to road salts. Road salt increases the vulnerability of birds to car strike and may poison some birds directly. To relieve thirst, birds may ingest snow which could have negative energetic consequences; consumption of meltwater containing high concentrations of salt may increase salt ingestion rather than alleviating salt toxicosis. Road salt may also affect wildlife through its impact on habitat, with reduction in plant cover or community shifts that could affect wildlife dependent on these plants for food or shelter.

Ferrocyanides are very persistent but are of low toxicity. However, in solution and in presence of light, they can dissociate and form cyanide. In turn, the cyanide ion (as HCN) may volatilize and dissipate fairly quickly. The ultimate effects of ferrocyanides therefore depend on the complex balance between photolysis and volatilization, which in turn depend on environmental factors. Modelling studies undertaken in support of this assessment, indicate that there is some potential for certain aquatic organisms to be affected by cyanide in areas of high use of road salts, although the likelihood that sensitive organisms would actually be exposed for extended periods in roadside habitats is uncertain.

**Based on the available data, it is considered that road salts are entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity, and that constitute or may constitute a danger to the environment on which life depends. Therefore, it is proposed that road salts be considered "toxic" under Section 64 of the *Canadian Environmental Protection Act, 1999* (CEPA 1999).**

Future management should focus on key sources in areas where the assessment has indicated concerns. These relate to patrol yards, roadway applications, snow disposal and ferrocyanides.

The use of de-icing agents is an important component of strategies to keep roadways open and safe during the winter and minimize traffic crashes, injuries and mortality under icy and snowy conditions. These benefits were recognized by the Expert Advisory Panel on the second Priority Substances List (PSL), even as they recommended that this assessment of potential impacts on environmental organisms be conducted. Any measures developed as a result of this assessment must never compromise human safety; selection of options must be based on optimization of winter road maintenance practices so as to not jeopardize road safety, while minimizing the potential for harm to environmental organisms. Any action taken to reduce impacts on environmental organisms is likely also to reduce potential for contamination of groundwater-based drinking water supplies, which is clearly desirable.

Patrol yards: Key concerns relate to contamination of groundwater at patrol yards, discharge to surface water and effects on aquatic biota. In addition, overland flow of salty snowmelt waters can result in direct impacts to surface water and near-field vegetation. Based on surveys and reviews, salt losses from patrol yards are associated with loss at storage piles (which include salt piles as well as piles of sand and gravel to which salts have been added), and during the handling of salts, relating to both storage, and loading and unloading of trucks. The discharge of patrol yard washwater is also a potential source of salt loss. Measures should therefore be considered to ensure storage of salt and abrasives to reduce losses through weathering, management practices to reduce losses during transfers, and management of stormwater and equipment washwater to minimize releases.

Roadway application: Key environmental concerns have been associated with areas of high salt use and high road density. Regions of southern Ontario and Quebec and the Maritimes have the highest rate of salt use on an area basis and as such have the highest potential for contamination of soils and surface and groundwater by road salts as a result of roadway applications. In addition, urban areas in other parts of the country where large amounts of salts are applied are of potential concern, especially for streams and aquifers which are wholly surrounded by urban areas. In rural areas, surface waters receiving drainage from roadways may also be susceptible to contamination. Any area of Canada where splash or spray from salted roads can be transported through air pathways to sensitive vegetation are a potential

concern. Wetlands which directly adjoin roadway ditches and which receive sheet runoff in the form of salty snowmelt waters are also foci for management concerns. Therefore, measures should be considered to reduce the overall use of chloride salts in such areas. The selection of alternative products or of appropriate practices or technology to reduce salt use should be considered while ensuring maintenance of roadway safety.

Snow disposal: Key environmental concerns relate to eventual loss of meltwater into surface water and into soil and groundwater at snow disposal sites. Measures to minimize percolation into soil and groundwater and direct the release of salty snow-melt waters into surface waters which have minimal environmental sensitivity, or via storm sewers could be considered. Measures should also be considered to ensure sufficient dilution before release.

Ferrocyanides: This assessment indicates that there is a possible adverse exposure for the more sensitive aquatic vertebrates in areas of very high use of road salts. Risks could be reduced by reducing total salt use or reducing content of ferrocyanides in road salt formulations. To reduce the possibility of exposure, producers of road salts could consider reducing the addition rate of ferrocyanide to road salt. Any reduction in total salt use would be expected to result in an equivalent reduction in release of ferrocyanides.

## 1.0 INTRODUCTION

The *Canadian Environmental Protection Act, 1999* (CEPA 1999) requires the federal Ministers of the Environment and of Health to prepare and publish a Priority Substances List (PSL) that identifies substances, including chemicals, groups of chemicals, effluents and wastes, that may be harmful to the environment or constitute a danger to human health. The Act also requires both Ministers to assess these substances and determine whether they are "toxic" as defined in Section 64 of the Act, which states:

> ...a substance is toxic if it is entering or may enter the environment in a quantity or concentration or under conditions that
> a) have or may have an immediate or long-term harmful effect on the environment or its biological diversity;
> b) constitute or may constitute a danger to the environment on which life depends; or
> c) constitute or may constitute a danger in Canada to human life or health.

Substances that are assessed as "toxic" as defined in Section 64 may be placed on Schedule I of the Act and considered for possible risk management measures, such as regulations, guidelines, pollution prevention plans or codes of practice to control any aspect of their life cycle, from the research and development stage through manufacture, use, storage, transport and ultimate disposal.

Based on initial screening of readily accessible information, the rationale for assessing road salts provided by the Ministers' Expert Advisory Panel on the Second Priority Substances List (Ministers' Expert Advisory Panel, 1995) was as follows:

> The Panel recognized the benefits associated with the use of road salts. However, these substances have negative effects on the environment. Large volumes are released through road salting, particularly in Ontario, Quebec and the Atlantic Provinces. There is evidence of adverse local environmental effects to groundwater and to plant and animal life following exposure. Algae and benthic fauna have been shown to be particularly sensitive to changes in chloride ion concentrations, resulting in a reduction of fish populations. The Panel recognizes that there has been considerable progress in upgrading storage facilities. However, given the widespread exposure to these substances, and their release in large volumes into the Canadian environment, the Panel believes that an assessment is needed to determine their ecological effects.

The basis for inclusion by the Ministers' Expert Advisory Panel on the Second Priority Substances List of "road salt" was limited to environmental effects, and did not identify concerns with respect to human health. Humans are exposed to road salt principally through the contamination of roadside well waters, where chloride and sodium levels can be increased, and taste adversely affected. These elements are not considered toxic; in fact, the Canadian Drinking Water Guidelines for chloride and sodium are based on taste, which is affected at levels well below those that might be of concern for toxicity (Health Canada, 1996). Other substances contained in road salt, including ferrocyanide compounds and certain metals, are present only at trace levels.

With respect to the potential for health effects of road salt per se, an extensive literature search failed to identify any studies which were adequate to serve as the basis for a health risk assessment. Dermal exposure to concentrated solutions of road salt caused dermal irritation, but no sensitization, in one study (Cushman *et al.*, 1991). There is a single correlational study in which a statistical association between road salt use and mortality from a number of types of cancer in the United States was identified (Foster, 1993). However, in this study road salt use would have varied in parallel with a number of other factors; for example, larger amounts of salt are used in urban centres, where there is also more exposure to air pollution. There would also have been differences among states in smoking patterns, diet and a host of other factors. The design of this exploratory study does not permit adjustment for these other factors, many of which are more plausible causes of cancer than road salt.

In view of the focus of this assessment on environmental effects defined by the Ministers' Expert Advisory Panel and the extremely limited and inadequate data available related to the potential impacts of road salt on human health, this assessment solely addresses effects on the environment (i.e., the determination of whether road salt is "toxic" under paragraphs 64a) and 64b) of CEPA 1999).

Descriptions of the approaches to assessment of the effects of Priority Substances on the environment are available in a published companion document. The document entitled "Environmental Assessments of Priority Substances under the *Canadian Environmental Protection Act.* Guidance Manual Version 1.0 — March 1997" (Environment Canada, 1997a) provides guidance for conducting environmental assessments of Priority Substances in Canada. This document may be purchased from:

Environmental Protection Publications
Environmental Technology Advancement Directorate
Environment Canada
Ottawa, Ontario
K1A 0H3

It is also available on the Internet at www.ec.gc.ca/cceb1/eng/psap.htm under the heading "Technical Guidance Manual." It should be noted that the approach outlined therein has evolved to incorporate recent developments in risk assessment methodology which will be addressed in future releases of the guidance manual for the assessment of effects on the environment.

The search strategies employed in the identification of data relevant to assessment of potential effects on the environment (prior to May 2000) are presented in Appendix A. Review articles were consulted where appropriate. However, all original studies that form the basis for determining whether road salts are "toxic" under CEPA 1999 have been critically evaluated (entry and environmental exposure and effects).

Preparation of the environmental components of the assessment was led by B. Elliott under the direction of R. Chénier. The Assessment Report and the supporting documentation related to the environmental assessment of road salts were prepared by and reviewed by the Environmental Resource Group established by Environment Canada to support the environmental assessment:

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## 2.0 SUMMARY OF BACKGROUND INFORMATION FOR THE ASSESSMENT OF ROAD SALTS

### 2.1 Identity, properties, production and sources

#### *2.1.1 Substance characterization*

Road salts can refer to any salt applied to roadways for roadway maintenance. As outlined below, road salts are mainly used in Canada as de-icing and anti-icing agents during winter road maintenance but smaller quantities are also used as dust suppressants. "Salt" can refer to any compound consisting of the cation from a base and the anion from an acid and which is readily dissociated in water. Products, specific road applications and application rates are included in Table 1. While sodium chloride (NaCl) is by far the most frequently used road salt in Canada, other inorganic salts used in Canada include calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$) and potassium chloride (KCl). Few additives are used in Canada as part of road salt formulations; sodium ferrocyanide is the only product regularly added as an anti-caking agent. Organic salts and a few other products are essentially used in Canada for maintenance of airports and for plane de-icing. Abrasives such as sand are used for winter roadway maintenance; while these are not salts, chloride salts are frequently mixed with abrasives and, as such, abrasives can be a source of chloride salts to the environment.

This assessment focusses on the inorganic chloride salts used for roadway maintenance. This is based on consideration that:

1. the original recommendations of the Ministers' Expert Advisory Panel called for an ecological assessment of the most commonly used de-icing chloride salt;

2. sodium chloride and, to a lesser extent, calcium chloride, are by far the most commonly used salts on roadways in Canada; and

3. all inorganic chloride salts have broadly similar behaviour and effects in the environment. Notably, effects related to toxicity of chloride can be considered to depend on the cumulative input of all chloride salts.

In addition, public concerns have been expressed regarding to the use of ferrocyanide salts in formulations of road salts, notably given that, in solution, they can photolyze to yield free cyanide ions, which are highly toxic to aquatic organisms. Since ferrocyanides are commonly used in road salt formulations, their entry, exposure and effects are also considered as part of the assessment of road salts.

Organic salts are not used in Canada or are used in specific circumstances such as at airports rather than on roadways, and are not assessed in this report. While abrasives are used

in large quantities in Canada, the nature and potential for environmental effects of these compounds are distinct from those of road salts and are not considered in this assessment.

### *2.1.2 Physical and chemical properties*

The Chemical Abstracts Service (CAS) Registry numbers and physical-chemical properties of four inorganic salts (NaCl, $CaCl_2$, $MgCl_2$ and KCl) and ferrocyanide used as road salts are given in Table 2. The physical-chemical properties of these salts determine their transport, fate and mode of action in the different environmental compartments.

The eutectic temperature is the lowest freezing temperature that can be achieved for water by adding a given salt to it (Table 2). The greater the difference between ambient temperature and eutectic temperature, the higher the rate of melting (OECD, 1989). Thus, from the salts presented in Table 2, calcium chloride would produce the highest melting rate. The rate of reaction is observed to be approximately the same for sodium chloride and calcium chloride at temperatures between -1 and -4°C, but from -5°C downwards sodium chloride acts more slowly than calcium chloride, when equal quantities are applied (OECD, 1989). Salinity is defined as the total dissolved solids in water after all carbonates have been converted to oxides, all bromides and iodides have been replaced by chlorides and all organic matter has been oxidized (Stumm and Morgan, 1981). Since all road salts are chloride salts, chloride ($Cl^-$) is the principal contributing anion to salinity resulting from the application of these salts, but other contributing anions in the environment include $HCO_3^-$, $CO_3^{2-}$ and $SO_4^{2-}$. Cations which contribute significantly to salinity include $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$. Salinity is closely related to the total halide concentration which is often called chlorinity (*Cl*). The relation between the two is described by the empirically derived Knudson equation (Mayer *et al.*, 1999).

Ferrocyanide is a very complex anion of limited solubility composed of a central iron atom surrounded by an octahedral configuration of cyanide ligands.

### *2.1.3 Production and use*

Road salts (mostly NaCl) have been used as ice-disbonding and ice-melting agents in Canada since the 1940s (Perchanok *et al.*, 1991).

#### 2.1.3.1 Sodium chloride

The predominant chloride salt used as de-icer is sodium chloride, which constitutes about 40% sodium and 60% chloride by weight. Trace elements, including trace metals, may represent up to 5% of total salt weight. Substances potentially present include phosphorus (14–26 ppm), sulphur (6.78–4 200 ppm), nitrogen (6.78–4 200 ppm), copper (0-14 ppm) and zinc (0.02–0.68 ppm) (MDOT, 1993). Sodium chloride is the most commonly used road de-icing chemical in North America. World production of sodium chloride totalled 189 thousand kilotonnes in 1995. The largest producers of this salt are the United States (21%), China (15%), Germany

(8%) and Canada (7%) (Natural Resources Canada, 1998). The largest global market for sodium chloride is the chemical industry (60%), followed by table salt (20%) and road de-icing (10%) (CIS, 1994).

As of 1993, there were 12 manufacturers of sodium chloride in Canada, with 24 plants in seven provinces. Total nameplate capacity was 13 645 kilotonnes per year and total domestic production was 10 895 kilotonnes. A further 1010 kilotonnes were imported from United States and Mexico, making a total supply of 11 969 kilotonnes. Of this, Canada exported 3106 kilotonnes, mainly to the United States. Canadian domestic demand was 8863 kilotonnes (CIS, 1994). The largest market for sodium chloride in Canada is snow and ice control, which accounts for about half the domestic demand (4240 kilotonnes in 1993). Total amounts used for de-icing fluctuate from year to year depending on weather conditions (CIS, 1994).

#### 2.1.3.2 Calcium chloride

Calcium chloride is the second most commonly used road salt in North America. Calcium chloride is the leading chemical for dust suppression in Canada. Liquid calcium chloride is primarily applied to gravel roads to consolidate aggregates and control dust. Calcium chloride is also used to pre-wet salt or sand in winter highway maintenance and to stabilize road base mixtures after pulverization. Of these three uses, dust control accounts for approximately 97% of total use.

In 1995, there were three calcium chloride producers in Canada, with one plant in Ontario and four brine wells in Alberta. Total nameplate capacity for calcium chloride in Canada for that year was 629 kilotonnes. At that time, domestic production totalled 399.4 kilotonnes and 24.6 kilotonnes were imported, creating a total supply of 424 kilotonnes. Of this, 156 kilotonnes were exported while Canadian domestic demand was 268 kilotonnes. The total amount used in 1995 in road dust suppression and in road construction was 201 kilotonnes (CIS, 1996).

#### 2.1.3.3 Mixture of sodium chloride and calcium chloride

A de-icing mixture of 80% NaCl crystals and 20% $CaCl_2 \cdot H_2O$ flakes is produced (MTO, 1996). About 20% of Ontario municipalities with a population greater than 15 000 use such a mixture for de-icing because the calcium chloride accelerates the start of the melting action (Perchanok *et al.*, 1991). Sodium chloride pre-wetted with calcium chloride brine has been field tested in British Columbia and has been recommended for reducing total salt applications (Gooding and Bodnarchuk, 1994). The total amount used for roads in Canada is included in the above estimates for sodium chloride and calcium chloride.

### 2.1.3.4 Magnesium chloride

Although not recommended for dust control on roads, magnesium chloride is an alternative dust suppressant for use on material piles, road shoulders or material transfer ponds (OMEE, 1993). A magnesium chloride de-icer (70% water, 25% $MgCl \cdot H_2O$, 15% PCI corrosion inhibitor) is distributed in Canada (MTO, 1996; Young, 1996). No information was found concerning magnesium chloride production volumes in Canada but is likely quite low.

### 2.1.3.5 Sodium chloride and magnesium chloride

A de-icing mixture (80% NaCl, 5% $MgCl_2$, 15% PCI) was formerly available in Canada. As of 1993, there were no suppliers in Ontario (MTO, 1996). While other sodium chloride-based de-icing products exist which can contain magnesium chloride as well as some corrosion-inhibiting additives (MDOT, 1993), there is no evidence of current use in Canada.

### 2.1.3.6 Potassium chloride

There is no known use of potash in road de-icing; however, potash mine tailings containing 0.5 to 2% potassium chloride (the rest is primarily NaCl) are applied to Canadian roads for de-icing (CFI, 1997). The estimated total amount for 1996 of potassium chloride used for roads in Canada is 3.3 kilotonnes (CFI, 1997). No information was found concerning the production of KCl in Canada.

### 2.1.3.7 Brines

Oil field brine is a traditional dust suppressant composed of calcium, magnesium, sodium and chloride. Oil field brine is obtained as formation water generated from oil exploration operations at several locations in southwestern Ontario (OMEE, 1993).

### 2.1.3.8 Ferrocyanide

To prevent clumping of the chloride salts during storage and de-icing operations, sodium ferrocyanide and ferric ferrocyanide are commonly added to these salts in Canada. In the case of sodium chloride, sodium ferrocyanide is added in amounts of 30 to 124 mg/kg (Letts, 2000).

Sodium ferrocyanide is not currently produced in Canada. However, approximately 300 to 350 tonnes per year are imported from European and Asian manufacturers for use as an anti-caking agent. Road salt containing sodium ferrocyanide is used in Ontario, Quebec and the Atlantic Provinces. From Manitoba to the interior of British Columbia, the by-product salt from Saskatchewan potash mines which is used as road salt is not treated with sodium ferrocyanide. On the West Coast, rock salt imported from Chile is treated with sodium ferrocyanide at a rate of 60 mg/kg. The quantity of ferrocyanide used in various jurisdictions can be estimated from the amount of salt used and its average ferrocyanide content.

### 2.1.4 *Sources and releases*

#### 2.1.4.1 Natural sources

Natural sources of sodium chloride, calcium chloride, magnesium chloride and potassium chloride salts in the environment include weathering and erosion of rocks and soils, atmospheric precipitation and groundwater discharge. The composition of the rock material, relief and climate are important factors which largely control the rates of weathering and dissolution. In aquatic ecosystems, cations such as $Ca^{+2}$, $Mg^{+2}$ and $K^{+}$ are not uniquely associated with chlorides but can be derived from natural sources such as carbonates from soils and bedrock in the watershed (Mayer *et al.*, 1999). Igneous rocks and associated soils have generally lower salt contents than shales and limestones (Pringle *et al.*, 1981). The contribution of salinity from atmospheric sources is particularly important in the coastal maritime regions. Areas that are dry with low rates of precipitation, such as the Canadian Prairies, have landscapes that tend to concentrate salts in surface soils because of high net evapotranspiration losses from the land. Natural sources of salts in aquatic ecosystems are reviewed by Evans and Frick (2000).

Vegetation stores $Na^{+}$ and $Cl^{-}$ but they are as well easily lost by ion uptake, leaf washing and litter decomposition. Chloride, as sodium and potassium, is an important inorganic solute of osmotic regulation. Chloride concentration in the environment is not affected by chemical or biological reactions. Chloride does not adsorb onto particulate matter. Potassium ion tends to be the most constant quantity in animal cells. Calcium is the most reactive ion of all the major cations contributing to salinity; it is required as a nutrient in higher plants and is one of the basic inorganic elements present in algae. Magnesium is important in enzymatic transformations and is required by chlorophyll-bearing plants.

While ferrocyanides do not occur naturally in the environment, cyanide compounds are naturally occurring substances reported from over 2000 plant species (Conn, 1980). Sodium ferrocyanide and ferric ferrocyanide are highly stable and relatively immobile in the environment. When they are exposed to sunlight, the ferrocyanide complex decomposes and releases cyanide ions ($CN^{-}$) (Meeussen *et al.*, 1992a). Under natural conditions, the cyanide ion hydrolyzes to volatile hydrogen cyanide (HCN) molecule (Shifrin *et al.*, 1995).

#### 2.1.4.2 Anthropogenic sources

Anthropogenic sources of inorganic chloride salts include domestic sewage and industrial processes (Sonzogni *et al.*, 1983) such as effluent from the chemical and petrochemical industry (Johnson and Krauss, 1991), gas manufacturing and acid mine drainage (USEPA, 1973; Pringle *et al.*, 1981). Once these substances enter the environment, they remain in aqueous phase until their concentrations exceed their solubility products, when crystallization and subsequent sedimentation of mineral salts might occur.

Salts may be released to the environment during their production, mining, mixing, and bulk transportation and storage. Since these industrial sources are not all limited to ultimate use as road salts, they are not considered further in this assessment.

Ultimately, all road salts enter the environment as a result of:

- storage at patrol yards (including loss from storage piles and during handling);
- roadway application (including at or about the time of application as well as subsequent movement of the salts off the roadways); and
- disposal of waste snow.

Releases are therefore associated both with point sources (storage and snow disposal) and line sources (roadway application). The following sections will review material pertinent to entry into the environment, notably loadings (including amounts applied to roadways), disposal of waste snow and patrol yards.

## 2.2 Road salts loadings

This section summarizes findings in a report prepared by Morin and Perchanok (2000) which characterizes the use of road salts in Canada. Information describing application rates and annual mass loadings per highway length and per geographic district area is provided. These detailed, geographically based data were used to calculate exposure and other information to support subsequent sections of the assessment. Data in this section focus on the use of sodium chloride and calcium chloride salts; magnesium chloride and potassium chloride salts are also used, but to a lesser extent. Industry representatives estimated that approximately 25 000 to 35 000 tonnes of magnesium chloride and 2000 tonnes of potassium chloride are used for roadway de-icing activities in Canada annually.

### *2.2.1 Survey responses*

Information on the use of road salts in Canada was obtained from recent surveys conducted by the Transportation Association of Canada (TAC), the Ministry of Transportation of Ontario (MTO) and Environment Canada (EC). The EC survey included data from provinces, municipalities and the private sector. Details and the methodology used in the surveys are presented in Morin and Perchanok (2000).

*Provinces*

Information on salt loadings and road network length were obtained from all provincial and territorial departments of transportation. The 1997–98 winter had the most complete data nation-wide; these data were used to estimate total salt use. Comparisons between data from salt suppliers and survey data suggest that the quantities reported are reliable (Morin and

Perchanok, 2000). After cross-referencing data on salt loadings, they were mapped by provincial maintenance district.

*Municipalities and regional governments*

Information was obtained from 104 municipalities across Canada. Data on salt use were also obtained from all regional municipalities and counties in Ontario. Some indicated salt use and road network length for each of the past five years; others provided information on salt usage for the 1997–98 winter.

*Salt industry data*

Salt suppliers provided purchase and tender data for 500 municipalities in Canada. A comparison between tender data and purchase data indicates a strong concordance between the two.

*Municipal estimates*

Despite the good response rate to the surveys, two limitations are related to the estimation of municipal de-icing salt loadings. First, information on salt usage by road type is available only for 104 municipalities. Second, even by combining data obtained from municipalities and salt suppliers, this does not represent total municipal salt use. Estimates were made to account for salt use by municipalities where no data were submitted.

Population was chosen as the variable to predict municipal salt use. This was done by deriving an average annual loading per person for municipalities with survey or purchase/tender data, and multiplying this by the population of all other municipalities in a maintenance district. By summing known municipal salt use and estimated municipal salt use, it was possible to estimate total municipal salt use by maintenance district. After estimates were made, salt use was mapped by maintenance district.

*Provincial and municipal use of dust suppressant salts*

The major producer provided market estimates of calcium chloride use on roadways by province. Recommended application rates for calcium chloride were obtained from industry. Rates vary depending on the type of gravel road, traffic and policies regarding roadway maintenance. Minimum and maximum loadings for a gravel road 7.4 metres wide were calculated.

### *2.2.2 Results*

Detailed results are presented in Morin and Perchanok (2000).

Provincial road network characteristics – saltable roads

Using survey information, maps depicting the distribution of provincial roads were created. Figure 1 shows total length of two-lane saltable road (freeways, paved and surface-treated roads) by maintenance district. A provincial road network area fraction was also calculated and mapped. Figure 2 indicates the area of saltable road maintained by provincial agencies per district area. This map can be used to estimate salt loadings to surface water in drainage areas of a similar size and shape. Districts with the highest proportion of saltable road to district area are in the Maritimes, southern Quebec, southern Ontario and parts of British Columbia.

### *2.2.3 Sodium chloride*

*Recommended application rates*

Information on recommended provincial application rates is depicted in Figure 3, while rates for select municipalities are in Figure 4. Application rates cannot be used to quantify annual loadings; they provide information only on the quantity of salt applied with each application, not the number of applications. Loadings presented in the rest of this section refer to average total annual mass, not application rates.

*Loadings*

Detailed data were analyzed separately for provinces, municipalities and regional governments, including calculations of mass of salt per length and surface area of two-lane saltable roads and per area of maintenance district (Morin and Perchanok, 2000). Areas with highest loadings were in central and southern Ontario and Quebec, followed by the Maritimes; lowest loadings were in the Prairies.

*Total sodium chloride loadings*

Municipal loadings were combined with provincial and territorial loadings to estimate total salt use by maintenance district for the 1997–98 winter season (Figure 5); it is estimated that 4 418 462 tonnes of sodium chloride were used as de-icers on roadways in Canada. In Figure 6, total loadings per maintenance district were normalized based on surface area.

Above estimates of total loading include data only on the use of road salts by municipal, provincial, territorial and regional governments. Private contractors, industry and agencies such as port and transit authorities also use road salts. Cheminfo (1999) estimated that total use by commercial and industrial customers is 5 to 10% of the road salt market. A midpoint value of 7.5% was used to estimate the quantity of road salts used by commercial and industrial sources in Canada (Table 3). If these quantities are included, it is estimated that 4 749 847 tonnes of sodium chloride road salts were used during the 1997–98 winter season.

### *2.2.4 Calcium chloride*

The quantity of calcium chloride used by province and territory is listed in Table 4. While Ontario is the province where the largest quantity of calcium chloride is used on roadways, analyses indicate that Nova Scotia is the province with the highest usage per unit area of land.

Total chloride loadings

Estimates on the quantity of sodium chloride and calcium chloride used on roadways in Canada are combined to estimate total chloride use on roadways by province, based on the atomic weights of the salts and the percentage chloride in each chemical. Table 5 presents total chloride use by province, based on total sodium chloride loadings for the 1997–98 winter season, and the estimated use of calcium chloride in a typical year. Mass of chloride used per area of province was calculated to provide a basis on which to compare loadings. Thus, while Ontario and Quebec are the provinces where the most chloride is used on roadways, Nova Scotia has the highest loading per unit area of province.

### *2.2.5 Reliability of loadings data*

Although a concerted effort was made to obtain data from the most accurate sources, error in data and the calculations are possible. It is possible that the quantity of materials spread was inaccurately recorded or that there is non-reported salt usage. There could also be inconsistencies in the data that were provided. For example, some provinces pay for municipal salt or maintain municipal roads. Hence, municipal data may be included in the provincial loadings for certain districts. Another problem could be that survey data refer to salt purchased and not salt used. While all the salt purchased will eventually be used, there is no way of determining the quantity of salt that is loaded on the system each year.

Potential errors with data from salt suppliers were assessed by correlating provincial bids and usage. Overall, both data sets are highly correlated. One possible source of error could be the use of 1997–98 data to characterize salt loadings. While these quantities are a best estimate, available provincial data indicate how loadings varied by maintenance district for the past five years. A potential limitation may be the use of a "saltable" category to characterize road salt loadings. Since highways generally receive higher loadings, it could be argued that the saltable category underestimates salt loadings on high-volume roads. Another limitation may be the use of population to estimate salt loadings for municipalities with no data. While there is a good correlation between municipal population and salt use at the provincial level, the strength of this relation varies by maintenance district.

Despite these potential limitations, data presented are good indicators of the quantities of salt used on roadways in Canada. This is particularly so when considering there is a

difference of 9.4% (417 501 tonnes) between known and estimated usage for the 1997–98 winter.

### *2.2.6 Conclusions*

The estimated annual use of sodium chloride road salt and calcium chloride dust suppressant salts in Canada was determined from a survey sent to provincial, territorial and municipal agencies, industry data, and estimates based on population. It is estimated that approximately 4 750 000 tonnes of sodium chloride de-icers were used in the 1997–98 winter and that 110 000 tonnes of calcium chloride are used on roadways in a typical year. When combined, it is estimated that 2 950 000 tonnes of chloride were used on roads in Canada during the 1997–98 winter season. It is recognized that amounts used will vary on a yearly basis, notably because of variation in climatic conditions.

Annual loadings of de-icing salts have a geographic trend with the highest loadings on a length of road basis occurring in Ontario and Quebec, intermediate loadings in the Atlantic Provinces and lowest loadings in the Western provinces. Error in loadings data was estimated where possible by comparing provincial or municipal data with product sales records; good correspondence was shown.

## 2.3 Disposal of waste snow

Delisle and Dériger (2000) reviewed available data on methods for disposal of snow, on the physicochemical and ecotoxicological characterization of waste snow, and on the environmental impact of disposal of waste snow in Canada and internationally.

### *2.3.1 Volumes of snow in Canadian cities*

Removal and disposal of snow may be required when accumulation of snow on or along roadways may hamper circulation or safety. As such, both snow volumes and extent of urban development affect the quantities of snow to be disposed (Table 6). Given the large amount of snowfall (annual snowfall of 200–350 cm in southern Quebec) and the size and density of the city, the winter snow volume for the City of Montreal alone was about 11 258 000 $m^3$ in 1997–98, compared to 1 500 000 $m^3$ for Toronto (before municipal amalgamation), and a total of more than 30 million cubic metres of snow each year for all municipalities in Quebec.

### *2.3.2 Snow clearing and snow disposal methods*

Clearing of snow generally involves plowing to the side of the roadway. In cities, snow clearing can begin as snowfall reaches 2.5 cm, with the snow being pushed to the sides of the streets and sidewalks. However, when the snow is particularly heavy (more than 10 cm) or when accumulation of snow on or beside roadways and sidewalks requires it, removal and disposal

begins with the snow being blown into trucks and transported to various disposal sites (City of Montreal, 1996). The various snow disposal methods have been reviewed by Delisle and Dériger (2000) and can be grouped into three categories:

2.3.2.1 Methods not involving snow removal

- pushing to the side of the road
- blowing onto land adjacent to roadways

This consists of pushing snow to the side of the road and, as required and appropriate, blowing it onto neighbouring land. Such disposal methods cannot be applied to municipalities with a high land occupation factor (LOF) (Delisle, 1994). It is the most prevalent approach to clearing of snow from roadways in non-urban areas.

2.3.2.2 Methods involving dumping into waterways after processing or treating meltwater

- surface or quarry dumps with on-site treatment or linked to a purification plant
- sewer chutes linked to purification plants
- snow melters equipped with a self-contained treatment system or linked to a purification plant

All these methods involve the ultimate release of the snow water to surface water, but involve some form of processing of meltwater. If the treatment plant uses a biological treatment system, dumping waste snow or meltwater into sewers can lower the waste water temperature, dilute the organic load and add chlorides and heavy metals to the sewer water, which can affect the biological purification process. Addition of large volumes of snow meltwater may be most appropriate for municipalities mainly serviced by an integrated sewer network (combined storm and domestic sewer), with treatment plants equipped with a physicochemical system that functions independently from the treatment process and which can therefore handle large volumes of both rainwater and snowmelt water from their streets. It is therefore probable that the addition of more snowmelt water will not affect the plants' day-to-day operations (Government of Quebec, 1991).

While releasing to municipal wastewater systems and subsequent treatment may remove some contaminants present in waste snow, ions such as chloride are generally not removed by water treatment systems (Deschamps and Cegka, 1997), although mixing with other wastewater may result in dilution.

*Surface snow dumps and quarry sites*

Disposal at surface snow dumps or quarries involves piling the snow on land with a slight slope while waiting for the spring thaw. Dumping snow on the ground constitutes in itself an initial treatment of the snow, since, after the snow melts, debris, suspended solids and heavy metals

stay on the site or in the adjoining drainage ditch (Government of Quebec, 1991b). Generally, dumps are on impermeable or slightly permeable ground or must be equipped with a geomembrane, and are equipped as necessary with a sedimentation facility or designed to direct the meltwater toward a waste water treatment system.

*Sewer chutes*

Snow disposal through sewer chutes linked to municipal sewer networks uses existing infrastructure and offers lower transportation costs from loading to unloading points. These are used in Montréal. Sewer chutes consist of a ground-level opening (loading shaft) sufficiently large to receive a full load and a vertical shaft that links the opening to either a main or interceptor sewer pipe. Power-operated, variable speed, continuous-flow snow chutes can be used with low-capacity sewer networks (Godbout, 1996; Couture, 1997).

*Snow melters*

The underlying principle of this disposal method is to dump water rather than snow into the sewer system. Melters can be stationary or mobile. The snow is dumped by trucks into preheated water tanks equipped with oil or gas burners. The City of Toronto uses this technique occasionally. So-called "geothermal" snow melting, using geological formations as a natural storage reservoir for water during the summer and keeping the water sufficiently hot to be able to melt the snow during the winter, has been used since January 1998 in Cap-Rouge, Quebec (Bilodeau, 1999).

2.3.2.3 Methods involving release to surface water without water treatment

- direct dumping into a waterway or onto its banks
- sewer chutes not linked to purification plants

This involves release of waste snow and any contaminants it contains to surface water either directly (water dumps into rivers or into the ocean), with some removal of large debris (dumping on banks) or with possible dilution by storm water (sewer chutes not linked to treatment plants).

### *2.3.3 Use of disposal methods by Canadian municipalities*

The use of snow disposal approaches by selected Canadian municipalities is shown in Table 7 (Delisle and Dériger, 2000). The huge volumes of waste snow in Montréal require several disposal methods. For its winter 1997–98 disposal operations, Montréal used surface dumps (7 sites), sewer chutes (11 sites), dumping into the St. Lawrence River (3 sites) and quarry dumps (2 sites) (City of Montreal, 1998).

Surface dumps are clearly the most common method of disposal in Canada. For example, Regina (Regina, 1997) uses between two and five surface dumps depending on the year. In the case of the Regional Municipality of Ottawa-Carleton, several studies have been conducted to determine the number of surface sites needed to accommodate waste snow in that region (McNeely Eng., 1990; McNeely-Tunnock Ltd., 1995). In a few instances like St. John's, Halifax and Vancouver, the snow is dumped into the sea at harbours. The direct dumping of snow to fresh surface water is restricted and will not be permitted at all in Quebec as of 2002. The use of snow disposal methods can change. In the past, municipalities such as Montréal used blowing onto private property and, occasionally, snow melters. Blowing on private land was virtually abandoned by Montréal because of social and political pressure and snow melters proved to be too expensive to operate because of high fuel costs (City of Montreal, 1996).

In certain cities like Halifax, large quantities of de-icing salt are used but little snow is removed; roadway meltwater is channelled to storm sewer systems. In fact, from 1996 to 1998, Halifax has done no snow clearing at all except for pushing the snow to the side of the streets and roads. If traffic or population safety problems develop, the snow is dumped into Halifax harbour (Delisle and Dériger, 2000).

### *2.3.4 Waste snow characterization*

While road salts may be responsible for the presence of sodium, chloride and cyanide ions in snow, major contaminants found in urban snow include debris; suspended solids (SS); oil and grease; ions [chlorides (Cl), sodium ($Na^+$), calcium ($Ca^{++}$)] and metals [lead (Pb), manganese (Mn), iron (Fe), chromium (Cr)] (Government of Quebec, 1997b). Concentrations of chlorides in waste snow or its snow melt for certain Quebec municipalities have ranged from 3.8 to 5689 mg/L (see Delisle and Dériger, 2000).

Chenevier (1997) recently compared average values for the physicochemical parameters analyzed in the waste snow from Montréal's primary and secondary streets in 1997. Concentrations for all parameters were higher for the primary streets; the secondary streets showed statistically lower levels for 7 of the 23 parameters: nitrates, cyanides, suspended solids, turbidity, chemical oxygen demand, pH and inorganic phosphorus. Concentrations of chloride were 3115 mg/L for secondary streets and 5066 mg/L for primary streets (Delisle *et al.*, 1997a), possibly reflecting higher frequency or rates of application of road salts.

The characteristics of waste snow depend on a wide range of factors, including source-community size, LOF, traffic density, quantities of de-icing salt and abrasives used, and duration of snow clearing (Malmqvist, 1985; Delisle, 1995). Contaminant content generally increases with time. For example, concentrations of chloride increased from 5 mg/L in snow from rooftop collectors to 530 mg/L after 72 hours for snow from residential city streets and 7496 mg/L after 72 hours for snow from commercial city streets (Delisle and Leduc, 1987), with concentrations

subsequently diminishing to 590 after more than one week, presumably due to loss of ions though meltwater.

### *2.3.5 Discussion*

In addition to inorganic ions from road salts, waste snow can contain a broad range of physical and chemical contaminants. Chloride ions are dissolved in and ultimately transported in meltwater, and are largely not affected by physical or biological water treatment. Impacts would therefore depend on total amounts and concentrations of the ions at the point of release of meltwater into surface water (storm sewers or wastewater treatment sites) or into soil and groundwater. While concentrations in waste snow and its meltwater can be quite variable, they can be as high as 5700 to 7500 mg/L.

## 2.4 Patrol yards

Patrol yards (also referred to as storage yards or maintenance yards) are used to store road maintenance materials before their application to roadways, and are therefore sources of contamination to the environment. The following sections describe and characterize these facilities, outline environmental exposure pathways, and present measured concentrations from specific points around patrol yards. Most of the data are based on pre-1998 standards for design and management of road salts. While more effective designs are currently being promoted to reduce salt loss, current design and management are largely similar to those considered in this assessment. Data in the following sections were summarized from a report prepared by Snodgrass and Morin (2000).

### *2.4.1 Number of patrol yards and quantity of materials stored*

Data compiled by Morin and Perchanok (2000) were used to estimate the number of provincial and territorial patrol yards and the quantity of road salts and abrasives stored at these yards. Assuming that total salt and abrasive use by jurisdictions are distributed equally among patrol yards, the average quantities used at patrol yards was estimated (Table 8). This table does not include municipal and county yards, and storage facilities used by private contractors, and hence significantly underestimates the number of maintenance yards in Canada. The number of patrol yards by district and the average tonnage of sodium chloride and abrasives that would be used by patrol yards for selected provinces is presented in Snodgrass and Morin (2000).

Data on the quantity of sodium chloride used for the winter of 1997–98 were obtained for 117 patrol yards that are administered by the MTO. It is estimated that the quantity of sodium chloride used at patrol yards ranges between 45 and 21 400 tonnes per yard; abrasive use ranges between 10 and 13 200 tonnes per yard.

### *2.4.2 Patrol yard design and management*

Patrol yards can be located in a variety of settings, and patrol yard design and standards vary substantially across Canada. Facilities used to store road salt can include domes/igloos, sheds and lean-tos; doors or walls may or may not be present, and storage under an overpass can be considered as covered by some agencies. The degree of protection against weathering offered by these facilities varies considerably. Salt may be stored on asphalt or concrete pads, or may be stored outside on a thick plastic tarp and covered by another tarp. While storage in buildings or other covered facilities can protect from precipitation which leaches the salt, there is no universal standard design for storage facilities. In addition to the type of facility used to store road salts, best management practices that promote good housekeeping at patrol yards are equally important to reduce salt loss. The effectiveness of best practices, however, depends on the rigour with which they were implemented.

#### 2.4.2.1 Salt-handling operations at patrol yards

Salts can be released from mixed abrasive piles as well as from salt piles. A mixed abrasive pile, whether composed of sand or gravel, is mixed with salt to prevent the abrasive from freezing and to keep abrasives in a flowing state (NB DOE and DOT, 1978). The percentage of salt varies — most agencies have 5% mixtures, but can range between 2.5 and 15% salt. A New Brunswick study (NB DOE and DOT, 1978) monitored the quantity and quality of leachate from a 2000-tonne abrasive pile with a 2.5% salt content. During the first year, 420 $m^3$ of leachate passed through the monitoring system. Sodium and chloride concentrations in the leachate are depicted in Figure 7. The maximum concentrations for sodium and chloride were 37 000 and 66 000 mg/L, respectively. It was estimated that total salt loss through leaching during the first year was 18.2 tonnes, or over a third of total salt added to the pile, even though 80% of the abrasive pile had already been removed for sanding operations by the end of January. Results of the second year also indicated high chloride concentrations in leachate from the pile. A total of 255 $m^3$ of leachate was measured. Sodium and chloride concentrations in the leachate are depicted in Figure 8. The maximum concentrations for sodium and chloride were 49 000 and 82 000 mg/L, respectively. Considering these concentrations and results of a survey which suggested that few provincial agencies cover mixed abrasive piles (TAC, 2000), the potential for salt loss from mixed abrasive piles is high.

Spillage during stockpiling and loading of spreaders is a major source of salt loss (TAC, 1999). A review of electro-magnetic surveys done at patrol yards indicated that spillage can be an important source of salts to the environment (Snodgrass and Morin 2000). These surveys, which typically identify subsurface materials and groundwater (within 6 m of the surface) that are highly conductive (e.g., soils and groundwater with elevated levels of salts), indicated high conductivity in areas adjacent to driveways and around storage facilities where salts are handled.

Winter road maintenance vehicles are regularly washed to minimize corrosion, and the washwater can be a source of salt to the environment. At patrol yards in urban areas, the washwater is likely released to a municipal sewage treatment system; in rural areas, discharge is probably to a dry well and left to percolate through the soil. In one study, washwater samples from seven patrol yards had chloride concentrations between 3500 and 37 000 mg/L; the average concentration was 16 000 mg/L (Beck *et al.*, 1994). This study also estimated that between one third and two thirds of patrol yards in Ontario discharge washwater to dry wells. Chloride concentrations in washwater can also be estimated by analyzing chloride concentrations in oil/water interceptors. These devices have been installed at some patrol yard garages to remove oils, greases and similar compounds from washwater waste streams. Since oil-water interceptors do not remove salt, concentrations in discharges will be the same as the influent. A study by INTERA (1996) indicated chloride concentrations in oil-water interceptors at three patrol yards ranged between 1100 and 35 400 mg/L.

### *2.4.3 Estimation of salt loss from patrol yards*

Estimation of salt loss at patrol yards and comparisons of this loss to the total amount of salt applied to roadways is addressed in the following section. Details of the assumptions used to calculate this loss are in Snodgrass and Morin (2000). Estimates of loss to the environment were made for an individual patrol yard, then total loadings to the environment were made assuming 190 active yards. Total estimated loss at patrol yards was then compared to a total roadway application of approximately 590 000 tonnes annually. This hypothetical scenario corresponds roughly to a major province or several smaller provinces as the aggregate basis for the calculations.

Table 9 provides three estimates based on the following scenarios: (1) a patrol yard with best management practices where salt and mixed abrasive piles are stored indoors; (2) a patrol yard where salt piles are stored indoors and abrasive piles stored outdoors; (3) a patrol yard where neither abrasive nor salt piles are stored indoors. Of the three scenarios, option two is probably most representative of patrol yards. The last column of Table 9 estimates the percentage of total road salt use that may be lost at patrol yards. Depending on the facility, and salt management options, 0.2 to 20% of total salt use can be lost at patrol yards.

### *2.4.4 Concentration at surface points around patrol yards*

A limited database for surface drainage systems around patrol yards is available from environmental site assessments (ESA) done at some MTO patrol yards (MTO, 1993–1999). Chloride concentrations at 29 yards where samples were taken ranged between 4 and 4880 mg/L; the mean chloride concentration was 659 mg/L.

A similar study was done for a yard in Alberta. A sample taken from the evaporation pond located on this property had a chloride concentration of 32 100 mg/L (Alberta Infrastructure, 2000). A study by Nova Scotia Transportation and Public Works indicated that

runoff and shallow groundwater flowing from a patrol yard to a small brook increased chloride concentrations in a small pond located approximately 250 metres downgradient from less than 75 mg/L to approximately 1000 mg/L (Rushton, 1999).

#### 2.4.4.1 Chloride concentrations in patrol yard wellwater

A study by (MTO, 1997) (change the Student *et al* 1997,1999 to read Ministry of Transportation of Ontario, 1997 - same title) (1997, 1999) graphed chloride concentrations from over 300 patrol yards in Ontario over a 20- to 30-year period ending in 1988. A 5-year period, 1982–88, was selected to characterize the range of concentrations that could be observed in patrol yard wells. Of the yards in the analysis, most (229 yards, 74%) had chloride concentrations below 200 mg/L. A smaller number of yards (82 yards, 26%) had concentrations above 200 mg/L, including 30 yards (9%) with concentrations greater than 500 mg/L and 14 yards (4%) with concentrations greater than 1000 mg/L.

ESAs done for patrol yards in the MTO's Eastern Region tested the quality of water in potable water wells (MTO, 1993–1999). Concentrations of chloride in samples from 36 wells ranged between 1.5 and 5050 mg/L; the mean concentration was 722 mg/L. Sixty-four percent of the samples had chloride concentrations greater than 100 mg/L, and 50% of the samples had chloride concentrations that exceeded 250 mg/L. Thirty-five percent of the samples had concentrations greater than 500 mg/L. Depth of the wells sampled range from 12 to 113 metres, with an average depth of 39.2 metres. Well construction can affect whether salts enter by leaching through soil or by local surface drainage, which flows down around the well casing to the well point.

#### 2.4.4.2 Chloride levels in patrol yard soils from site audit database

Data from ESAs (MTO, 1993–1999) can be used to assess the effect of patrol yard operations on soil quality. At several patrol yards, test pits and bore holes were dug and soil samples were analyzed. Chloride concentrations from 53 test pits ranged between 5 and 14 500 µg/g soil; sodium concentrations for 46 samples ranged between 39 and 13 100 µg/g soil. The average concentrations for chloride and sodium were 2100 and 2600 µg/g soil, respectively.

Chloride concentrations in soil samples from 46 bore holes ranged between 2 and 13 300 µg/g soil. The average chloride concentration was 1500 µg/g soil. Sodium concentrations for 98 samples ranged between 86 and 6720 µg/g soil; the average sodium concentration was 870 µg/g. Bore holes were between 0.1 and 5 metres deep, with an average depth of 1.6 metres.

#### 2.4.4.3 Chloride levels in groundwater monitoring for site audits

The same set of ESAs (MTO 1993–1999) was also used to assess the quality of shallow groundwater. At several patrol yards, monitoring wells were installed to depths ranging between

0.26 and 5.25 metres and groundwater was sampled. Chloride concentrations ranged between 1 and 24 000 mg/L; the mean chloride concentration for the 102 samples was 2600 mg/L. A summary of the data indicated that 75% of the samples had chloride concentrations greater than 100 mg/L, and 69% of the samples had chloride concentrations that exceeded 250 mg/L.

In similar types of analyses, chloride concentrations in groundwater at three Alberta patrol yards ranged between 26 and 26 400 mg/L (Alberta Infrastructure, 2000), and chloride concentrations in groundwater at three patrol yards managed by Nova Scotia Transportation and Public Works ranged between 254 and 38 600 mg/L (personal communication, Rushton, 1999).

#### 2.4.4.4 Off-site impacts at patrol yards

A review of select case studies by Morin (2000) indicated that there have been off-site impacts at several locations where road salts are stored. A few examples are presented in the following paragraphs.

Arp (2000) examined how the presence of a salt depot can be associated with elevated levels of salinity in surface waters. Sodium concentrations in areas surrounding the depot varied by type (ditch and stream water) and by location. Sodium concentrations were highest at and near the salt depot, ranging from 3000 to more than 10 000 mg/L. Runoff and seepage from the depot was quickly diluted by flowing surface water next to the depot, down to about 100 to 300 mg/L sodium. There are also seasonal variations: salt concentrations near the salt depot are lowest during snow melts and the rainy fall season. During summer, salt concentrations increase with reduced precipitation and increasing air temperature. Highest concentrations occur in June, July and August. At this time, the high salt concentration envelope that surrounds the salt depot spreads into the adjacent pond, and causes elevated salt concentrations in the main drainage stream.

Exposed abrasive piles and salt reserves stored in sheds that offered poor protection from the elements resulted in the contamination of the municipal water supply for Heffley Creek, British Columbia (BC-MoTH, 1993). Historically, road salts had been stored at this site since 1973. Abrasives piles with a 3% salt mixture were also stored at this site in unprotected piles (AGRA, 1995). In 1993, the B.C. Ministry of Transportation and Highways received an official complaint from the Municipality of Heffley Creek that groundwater for one of its two wells had been contaminated by road salts which were stored at the Heffley Creek patrol yard. By 1994, there were elevated concentrations at both municipal wells which are located between 175 and 200 metres from the Heffley Creek patrol yard (Figure 9). While chloride concentrations have decreased since 1996, well # 1 still has concentrations that are higher than 250 mg/L.

In 1996, complaints were registered with NS-DTPW and NS-DOE regarding salt contamination of residential wells in Bible Hill. Tests undertaken at three wells that supplied six

duplexes indicated that chloride and sodium concentrations ranged from 130 to 640 mg/L (personal communication, NS-DTPW, 1999). The Bible Hill patrol yard, which is located relatively close to these residences, was determined to be the source of salt contamination. While road salts are stored in a salt dome, abrasive mixtures have traditionally been stored outside. The NS-DTPW (Personal communication, 1999) indicated that this type of contamination was typical of locations where abrasive piles (mixed with salt) are left uncovered.

A study by Ohno (1990) conducted on wetlands near sand-salt storage sites in Maine showed that concentrations of chloride and sodium at the affected sites were two to three orders of magnitude higher than those of control sites. The concentrations at the control sites were 6 mg/L sodium and 8 mg/L chloride, while the concentrations at the affected sites ranged from 16 to 8663 mg/L sodium and 14 to 12 463 mg/L chloride.

Pinhook Bog, LaPorte County, Indiana, was adversely impacted by contamination from a salt-storage pile from the late 1960s to the early 1980s (Wilcox, 1982). Chloride concentrations at control sites in 1980 and 1981 were 5 to 6 mg/L. This compares to a maximum single daily reading for salt-impacted locations of 1468 mg/L chloride in 1979, 982 mg/L chloride in 1980 and 570 mg/L chloride in 1981. The total chloride inputs to the bog over the 10-year period when salt storage occurred were estimated as follows: 2.3 million kg from the salt pile, 0.4 million kg from road salting and 0.012 million kg from direct precipitation.

## 2.5 Environmental fate and pathways

In aquatic systems, chloride salts are present in dissociated form as chloride ions (Cl) and corresponding cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$). The chloride ion is extremely mobile: it does not biodegrade, does not easily react with other ions to form a solid, does not volatilize, is not involved in biological processes, and does not adsorb significantly on mineral surfaces (MDOT, 1993). The circulation of chloride through the hydrologic cycle is due mostly to physical rather than chemical processes. The chloride ions pass readily though soil, enter groundwater, and eventually drain into surface waters.

When water percolates through soil, positively charged ions (i.e., $Na^+$, $Ca^{++}$, $Mg^{++}$, $K^+$) are attracted to and bond with the inherently negatively charged soil surfaces. The extent of the bonding depends on the cation exchange capacity and the number of negatively charged sites in the soil. Elemental sodium has a high solubility and may, once dissolved, remain in solution, but since it is readily adsorbed on soil particles it is less probable it will reach groundwater and surface waters. Nevertheless, in cases where adsorption does not take place, or where leaching from the soil occurs, elemental sodium will follow water pathways and eventually find its way to groundwater and surface waters (MDOT, 1993).

In sodium ferrocyanide, the chemical bond between the cyanide group and the iron is very strong, but, in water, it can be photolyzed to release cyanide ions (Hsu, 1984). Laboratory

tests determined that a 15.5 mg/L solution of ferrocyanide would produce 3.8 mg/L of cyanide upon exposure to sunlight for 30 minutes (U.S. EPA, 1971).

Road salts released from **storage sites or patrol yards** will enter **soil** from:

- spillage of salts at storage sheds during stockpiling or transferring of chemicals or abrasives or during loading and unloading of maintenance vehicles;
- spillage of salts in the remainder of the yard as maintenance vehicles drive through;
- wind-driven erosion of salts from piles and from uncovered winter maintenance vehicles;
- precipitation or snowmelt waters which dissolve salts and infiltrate into the soil; and
- release from vehicle washwater discharging onto the soil.

Road salts released from **storage sites or patrol yards** will enter **surface water** from:

- overland runoff of storm water which has dissolved salts, from snowmelt water and vehicle washwater; and
- storm water pipage which drains part of the yard to a surface water body.

Road salts released from **storage sites or patrol yards** will enter **groundwater** from:

- groundwater recharge from soil and from surface water (see Section 2.2);
- releases from vehicle washwater where the effluent is discharged to a dry well; and
- entry through wells or around well casings.

Road salts released from **storage sites or patrol yards** will enter **air** from:

- wind-borne spray or splash.

Road salts released through **snow disposal** will enter **soil** and **groundwater** from:

- direct percolation of precipitation and meltwater from snow disposal sites.

Road salts released through **snow disposal** will enter **surface water** from:

- direct release in the cases of dumping into surface water, releases to untreated storm sewers, or melting following disposal on banks of water bodies;
- release via wastewater treatment plants in the cases of dumping to treated storm sewers or of surface disposal sites draining to treated water system;
- overland runoff of storm water and snowmelt water; and
- storm water pipage which drains part of the disposal area to a surface water body.

Road salts released through **snow disposal** will enter **air** from:

- wind-borne spray or splash.

The transport pathway for road salts applied to roadways is illustrated in Figure 10. Road salts applied to **roadways** can enter **surface water** from:

- direct runoff of road salts in solution from roads into drainage ditches, streams or wetlands soon after application. Factors affecting the degree of road runoff into aquatic ecosystems include: a) the length of major road treated and drained, b) the amount of salts applied prior to the thaw period, c) road drainage pattern and topography, d) level of discharge of the receiving stream, e) degree of urbanization, f) rate of rise and duration of temperatures above freezing and g) precipitation (Scott, 1981).

- the runoff of salt-contaminated snowmelt water some time after application of salts; and
- release of salts stored in surface soils (Scott, 1980).

Road salts applied to **roadways** can enter **soils** and **groundwater** from:

- meltwater and salt-contaminated precipitation from roadways.

Road salts applied to **roadways** can enter **air** from:

- wind-borne spray or splash; this can be affected notably by vehicle speed, wind, road gradient and geometrical features of the road (McBean and Al-Nassri, 1987).

Because they are persistent and are entrained in the hydrological cycle, all chloride ions applied to roadways as road salts or released from patrol yards or disposal sites can be expected to be ultimately found in surface water.

## 2.6 Spatial characterization of concentrations in surface waters

The information presented in this section resulted from a review of numerous agency reports, scientific publications and monitoring surveys prepared by Mayer *et al.*, (1999) and Evans and Frick (2000). This includes: 1) information on the physical/chemical properties of inorganic salts commonly used for road maintenance, 2) their fate and transport in surface waters and sediments, 3) environmental concentrations of constituents of road salts in Canadian surface waters in the context of watershed geology and other environmental factors governing their concentrations in surface waters, 4) a spatial map of chloride concentrations as a basis for developing an understanding of a spatially based, ecological risk assessment for surface water systems, and 5) relating the spatial risk map to observed concentrations of chlorides. The data suggest that the surface waters most sensitive to road salts impacts are small ponds and streams draining large urbanized areas.

The surface water ecosystems covered include running (lotic) waters, such as rivers and creeks, and standing (lentic) waters which include lakes, ponds and wetlands. Both the pelagic and the benthic compartments of these ecosystems will be discussed. Also presented is a review of background concentrations, and concentrations for waterbodies that have been impacted by the spreading of road salts. Examples of waterbodies that have been impacted by the storage of road salts were included in the section on patrol yards.

### *2.6.1 Fate/Transport*

Once these salts enter surface waters, they remain in solution, unless their concentrations are very high and exceed their solubility, when crystallization and subsequent sedimentation of mineral salts could occur. There are no major removal mechanisms such as volatilization, degradation (photodegradation, biodegradation), sorption (to particulates) or oxidation which would remove the salts from surface waters. Dilution resulting from mixing with low salinity water would decrease the salt concentrations in the aqueous phase. Hence, the salts will always be present in the aqueous phase rather than in the particulate phase (suspended or bottom sediments). In the case of benthic sediments, salts may accumulate in sediment interstitial water (porewater).

Dissolved salts, however, may alter the physical properties of water by changing its density. Density increases linearly with increasing salinity (Ruttner, 1963). The increases in the density resulting from salinity changes are large in comparison to density changes associated with temperature and have important implications for lakes, as inorganic salts can accumulate temporarily or permanently in deeper strata and prevent lake waters from mixing (Section 2.3).

The chemical and biochemical behaviour of major ions from four inorganic salts considered in this report is discussed, as their behaviour has important implications on their concentrations in surface waters and effects on aquatic biota.

#### 2.6.1.1 Chloride

Chloride is the principal contributing anion to salinity from application of road salts and is influential in general osmotic salinity balance (Wetzel, 1975; Hammer, 1977). Chloride is a highly soluble and mobile ion which does not volatilize nor does it easily precipitate or adsorb onto surfaces of particulates. In freshwater ecosystems, chloride behaves conservatively (i.e., its concentration in water is not affected by chemical or biological reactions) (Wetzel, 1975; Pringle *et al.*, 1981). Chloride levels in surface water will largely change only in response to addition of chloride, dilution by precipitation or in-flow, or concentration by evaporation of water. In the majority of inland surface waters, the concentrations of chloride and the respective cations rarely reach solubility products of the respective chloride salts, and so precipitation rarely occurs.

#### 2.6.1.2 Sodium and potassium

In surface waters, the monovalent cations sodium and potassium are relatively conservative in their chemical reactivity and low biotic requirements. Because of their conservative nature, the spatial and temporal distribution of sodium and potassium in unimpacted freshwater systems is uniform with little seasonal variation.

#### 2.6.1.3 Calcium

Calcium is the most reactive ion of all the major cations contributing to salinity. Its concentrations in surface waters are affected by chemical and biological processes within the aquatic systems. It is required as a micronutrient for higher plants and is one of the basic inorganic elements of algae. Calcium concentrations in hard water lakes undergo seasonal changes, with decrease in calcium concentrations and total alkalinity in the summer, when biogenically induced decalcification removes calcium from the water column. Decreased concentrations of inorganic carbon in the epilimnion, resulting from increased rates of photosynthesis, are responsible for the precipitation of calcium with bicarbonate, $HCO_3^-$. Some of the precipitated calcium carbonate is resolubilized in the hypolimnion and some is entrained in sediments. Decalcification of the trophogenic zone changes monovalent:divalent cation ratios, which has an effect on the distribution and dynamics of algae and larger aquatic plants in freshwater ecosystems (Wetzel, 1975).

#### 2.6.1.4 Magnesium

In general, magnesium compounds are more soluble than other compounds. In hardwater systems, calcium carbonates precipitate before more soluble magnesium carbonates. Significant precipitation of magnesium carbonate and hydroxide occurs only at very high pH (>10). Magnesium is a micronutrient in enzymatic transformations of organisms. It is required by chlorophyll-bearing plants as the magnesium porphyrin of the chlorophyll molecules (Wetzel, 1975). However, the metabolic requirements for magnesium are small in comparison to its availability in freshwater systems.

### *2.6.2 Environmental concentrations: Lakes and rivers*

In the absence of anthropogenic sources, surface waters acquire their characteristics by dissolution and chemical reactions with solids, liquids and gases with which they come into contact during various phases of the hydrological cycle (Stumm and Morgan, 1981). For instance, stream water chemistry can be related to the chemistry of the source rock and to equilibria controlling the formation of solid phases (Feth *et al.*, 1964; Garrels and Mackenzie, 1967). Watershed bedrock and surficial geology play, therefore, a major role in determining the salt concentrations in surface waters. In addition, the climate and the proximity of the surface waters to the sea will be important in regulating the background salt concentrations. Thus, the background salt concentrations (salinity) of surface waters vary.

Surface waters range from freshwaters, with salinities lower than 500 mg/L, to saline waters, with the salinities equal or greater than 3000 mg/L (Hammer, 1986). While enclosed lakes and ponds may become saline, streams and rivers will rarely have natural salinity high enough to be classified as saline.

For the purpose of this report, surface water quality is discussed by geographic regions rather than by the hydrogeological regions in order to better address the effects of human factors on surface water quality.

2.6.2.1 Atlantic Region (Newfoundland, Nova Scotia, New Brunswick and Prince Edward Island)

The median concentrations of chloride and calcium from recent surveys (1985 and later) were compiled by Jeffries (1997). The data set includes 38 lakes from Labrador, 63 lakes from Newfoundland, 150 lakes from Nova Scotia and 166 lakes from New Brunswick. The median chloride and calcium concentrations in lakes in largely unimpacted areas ranged between 0.3 and 4.5 and 0.82 and 1.10 mg/L, respectively.

Comprehensive studies of Kerekes *et al.* (1989), Kerekes and Freedman (1989) and Freedman *et al.* (1989) at the Kejimkujik National Park, Nova Scotia, investigated water quality of several lakes and rivers in the park. These studies concluded that sea salt influence is significant in Nova Scotia. The concentration ranges were 3.6 to 5.4 mg/L for chloride, 2.3 to 3.4 mg/L for sodium and 0.36 to 0.96 mg/L for calcium. The levels of these ions were comparable with those measured in other surface waters in the Atlantic Region (Jeffries, 1997).

Studies on the Chain Lakes near Halifax indicate that winter de-icing activities can have an impact on water quality. Thirmurthi and Tan (1978) explained that, from June to September 1975, the chloride concentration was approximately 19 mg/L. Concentrations began to increase in November and eventually peaked in May 1976, at 43 mg/L chloride. The chloride concentration then dropped rapidly through the rest of May and June, decreasing to 19 mg/L in July. The increase in chloride concentrations for both lakes represents an approximate addition of 19 440 kg of chloride to First Chain Lake and 7920 kg to Second Chain Lake.

The Chain Lakes continued to be studied through the early 1980s (Hart, 1985, 1988). Chloride concentrations in both lakes increased gradually from 1976 to reach a maximum in the mid-1980s of ca. 120 mg/L in First Chain Lake and ca. 170 mg/L in Second Chain Lake. Highest chloride concentrations were observed during spring runoff.

De-icing salts have impacted Chocolate Lake, in Nova Scotia. The lake is small (82.7 ha), shallow (mean depth = 3.9 m, maximum depth = 12.2 m), with an estimated volume of 350 000 $m^3$ (Kelly *et al.*, 1976). The watershed is large (900 ha), approximately 11 times as great as the lake surface area. Chloride concentrations were highly elevated in the lake between April and August 1975. Average summer chloride concentrations were 207.5 mg/L versus an

estimated background value of 15 to 20 mg/L for non-impacted lakes. Chloride concentrations varied with depth, ranging from 199 to 224 mg/L at the surface, from 189 to 217 mg/L at 6.1 m, and from 225 to 330 mg/L at 12.1 m. Sodium concentrations ranged from 108 to 125 mg/L, 102 to 125 mg/L and 116 to 183 mg/L at the same depths. The gradient in salt concentrations and the absolute concentration of salt in deep waters was large enough to prevent complete vernal vertical mixing of the water column; deep waters became anoxic in summer. The primary source of this excess chloride was attributed to highway de-icing salt runoff. Kelly *et al.* (1976) estimated that 64.2 tons (58 364 kg of road salt representing 35 409 kg of chloride and 22 737 kg of sodium) were applied to the Chocolate Lake drainage basin during the winter of 1974/75.

2.6.2.2 Central Region (Ontario and Quebec)

The concentrations of chloride, sodium and calcium in lakes and rivers in the Canadian Shield which covers a large area of Quebec and Ontario, including Upper Great Lakes, are very low (e.g., 1–10 mg/L chloride) (Jeffries, 1997). According to Weiler and Chawla (1969), the annual concentrations of chloride in Lakes Erie and Ontario were 24.6 and 27.5 mg/L, respectively, while corresponding chloride concentrations in Lake Superior were only 1.3 mg/L. Earlier studies (Kramer, 1964; Beeton, 1965; Dobson, 1967), which investigated water quality trends in the Great Lakes, reported a rapid increase in chloride concentrations related to human activities. The largest increase was observed for Lake Ontario. Later data (Williams *et al.*, 1998), however, showed a decline in chloride concentrations from about 22 mg/L in 1977 to about 16 mg/L in recent years (1985–1993). The decline in the Lower Great Lakes can probably be ascribed to lower loadings from industrial and domestic sources, resulting from improved control/treatment of industrial and domestic effluents. The tributaries to Lake St. Clair (e.g., Sydenham and Thames rivers) have somewhat higher chloride concentrations (about 30–40 mg/L) than other southern Ontario rivers because they drain the Paleozoic sedimentary rock adjacent to Michigan Basin which contains saline formations such as salt (NaCl) and anhydrite-bearing ($CaSO_4$) strata. These strata also contribute to salt inputs (NaCl and $CaSO_4$) to Lake St. Clair and Western Lake Erie.

In urbanized areas, application of de-icing salts contributes significantly to chloride inputs. Long-term monitoring locations in the Greater Toronto Area (GTA) show a gradual increase in chloride concentrations. In Highland Creek, a highly degraded urban watercourse, the statistical trend analysis shows an increase in chloride concentrations from 150 mg/L in 1972 (presumably already impacted) to over 250 mg/L by 1995 (Bowen and Hinton,1998). In Duffin Creek, the median chloride concentrations increased from 10 to 20 mg/L in the 1960s to 30 to 40 mg/L in the early 1990s (Bowen and Hinton, 1998). In urban streams and rivers, such as the Don River in Toronto, concentrations of chloride have increased to more than 1000 mg/L in winter (Scott, 1980; Schroeder and Solomon, 1998), with increases appearing to coincide with thaws. During snow storms or salt application, chloride concentrations as high as 89 000 mg/L were measured in the meltwater from some city streets. The autumn baseline values in the Don River were 100 to 150 mg/L of chloride. Similar baseline concentrations of chloride (50–100 mg/L) were reported in another Toronto creek, Black Creek (Scott, 1980). Chloride

concentrations 50 times higher than baseline values were measured during the thaw periods in this creek. Crowther and Hynes (1977) reported high winter concentrations of chloride (1770 mg/L), sodium (9550 mg/L) and calcium (4890 mg/L) in Laurel Creek which passes through urban Waterloo. Rodgers (personal communication) observed high concentrations of chloride (4355 mg/L) in Red Hill Creek, an urban stream in Hamilton, Ontario.

The MTO has monitored water quality in a number of streams in the province, including the Toronto Watershed. Three stations were monitored on Etobicoke Creek between 1990 and 1996 (Table 10). All these stations were located in developed areas, often near roads or highways and thus clearly impacted by road salt. The minimum chloride concentration ranged from 0 to 43 mg/L, the maximum from 2140 to 3780 mg/L, and the mean from 278 to 392 mg/L. Highest concentrations were observed in February followed by January, December and March. At the one monitoring station on Mimico Creek, minimum, maximum and mean chloride concentrations were 51, 3470 and 553 mg/L, respectively. Highest concentrations were observed in December followed by February, January and March. Similarly, minimum, maximum and mean chloride concentrations at Highland Creek were 22, 1390 and 310 mg/L and at Black Creek they were 20, 4310 and 495 mg/L, respectively. Highest concentrations were observed in December followed by February, January and March. Highest concentrations during the winter months are strongly suggestive of road salt inputs. Water quality frequently (180 — 62% of the measurements) exceeded 250 mg/L and often (8–22%) exceeded 500 mg/L.

Little Round Lake in central Ontario was affected by cultural disturbances that included urbanization, septic tanks, highway road salt runoff and seepage from a salt storage depot (Smol *et al.*, 1983). This small lake (7.4 ha, maximum depth 16.8 m) apparently became meromictic as a result of road salt runoff and localized storage. Salt concentrations in the monimolimnion or deep layer were 58.4 mg/L sodium and 103.7 mg/L chloride, well in excess of that explainable by the natural geology of the region. Road salt additions apparently resulted in the formation of meromixis some 30 years earlier.

The Ministry of Transportation of Quebec (MTQ) investigated the impacts of road salt on Lac à la Truite, near Sainte-Agathe-des-Monts (see Morin 2000). The lake drainage area, estimated at 728 ha, was affected by a 7-km stretch of highway (approximately 30-lane kilometres). The lake had a surface area of 48.6 ha, a mean depth of 21.5 m and an estimated lake volume of 486 000 $m^3$. In 1972, average chloride concentration for the lake was 12 mg/L. This increased through the 1970s to reach a maximum concentration of 150 mg/L in 1979. This corresponds to an addition of 67 068 kg of calcium salt to the lake. To prevent further increases, the use of road salts was replaced by abrasives (containing some salt to prevent caking). Chloride concentrations fell through the 1980s to reach 45 mg/L in 1990 and have remained at that level since.

The previous studies indicate that salt-laden runoff from roadways has the potential to adversely affect water bodies. A study by Mayer *et al.* (1998) characterized chloride

concentrations in runoff from roadways at three sites in southern Ontario: 1) the Burlington Skyway Bridge (a 4-lane road with 92 000 cars/day), 2) Highway #2 east of Brantfort (a 2-lane road with 31 100 cars/day), and 3) Plains Road in Burlington (a 2-lane roadway with 15 460 cars/day). Highest chloride concentrations (up to 19 135 mg/L) tended to be observed for runoff from the Skyway Bridge, although high concentrations also were observed at the Plains Road.

Although not in Canada, significant increases observed in chloride concentrations in four Adirondack streams were attributed to winter salt application (Demers and Sage 1990). There was a significant difference in chloride concentrations between samples upstream and downstream from roadways. Demers (1992) reported that chloride concentrations were as much as 66 times higher in downstream samples. The overall mean chloride level upstream was 0.61 mg/L and 5.23 mg/L downstream. The terrain characteristics of Adirondack streams (New Hampshire) are similar to those of streams in Eastern townships of Quebec. Chloride concentrations of 11 000 mg/L (Hawkins and Judd, 1972) were measured in winter of 1969 in Meadowbrook which drains about four square miles of suburbs in Syracuse, New York (Hawkins and Judd, 1972). Also in the United States, chloride concentrations of about 400 mg/L were measured in the bottom waters of Irodenquoit Bay, a small bay on Lake Ontario near Rochester, New York (Bubek *et al.*, 1971, 1995).

#### 2.6.2.3 Prairie Region (Manitoba, Saskatchewan, Alberta)

Most naturally saline lakes in Canada are located within two regions. The first region which encompasses several endorheic drainage basins is located on the Canadian Prairies (Hammer, 1984). The area where saline lakes are most numerous stretches over southern Alberta and Saskatchewan. The Alberta-Saskatchewan saline lake region is largely underlain by Cretaceous bedrock, composed mainly of shales, silts and sandstones (Hammer, 1984). Of the Prairie Provinces, Saskatchewan has by far the greatest number and volume of saline lakes (Hammer, 1986). The cationic proportions in most Prairie lakes are Na>Mg>Ca. Of the lakes investigated, there are only two known meromictic lakes on the Canadian Prairies, Waldsea Lake and Deadmoose Lake (Hammer, 1984). Numerous potholes (shallow lakes or ponds), which range in their salinity from fresh to saline, can be found in the southern prairies.

There are fewer naturally saline lakes (about 30) in Alberta (Hammer, 1984). Most of them are concentrated in the Provost and Hanna regions, although they occur as far north as Edmonton. Even fewer saline lakes are in Manitoba. Barica (1978) investigated a group of over 100 small potholes which varied in their salinity from fresh to moderately saline near Erickson in southwestern Manitoba. The concentration ranged (in mg/L) were 1 to 448 for chlorine, 0.8 to 1075 for sodium and 27 to 380 for calcium. Twenty-three sodium chloride–dominated sites along the western shore of Lake Winnipegosis were studied by McKillop *et al.* (1992). The concentration ranges for chloride, sodium and calcium were 861 to 33 750 mg/L, 587 to 21 313 mg/L, and 59 to 1400 mg/L, respectively.

Much lower concentrations of chloride and calcium are reported (Jeffries, 1997) for 27 and 193 lakes in northern portions of Saskatchewan and Alberta, respectively. The median concentrations of chloride were 0.2 and 0.5 mg/L, respectively. The calcium concentrations of Saskatchewan and Alberta lakes were 2.0 and 14.0 mg/L, respectively. The chloride and calcium concentrations of 26 lakes in Manitoba were 2.0 and 7.5 mg/L, respectively (Jeffries, 1997).

#### 2.6.2.4 Pacific Region (British Columbia)

The second region in Canada, where a large number of naturally saline lakes are located, is the Southern Interior Plateau (Fraser Plateau) of British Columbia, in the rain shadow of the Coast Mountains. Saline lakes in British Columbia are small and shallow (Topping and Scudder, 1977). The limnology of four of these lakes was described by Northcote and Halsey (1969) who showed that these lakes not only differed in total dissolved solids concentrations among themselves, but there were also differences within the lakes (surface to near-bottom). The surface and bottom chloride concentrations (in mg/L) were 5.1 and 7.1 mg/L, respectively, in Yellow Lake, 121 and 159 mg/L, respectively, in White Lake, 800 and 709 mg/L, respectively, in Mahoney Lake, and 7.9 and 419 mg/L, respectively, in Lyons Lake. Except for Yellow Lake, the meromixis in these lakes was maintained by chemical density gradients; in Yellow Lake, the mixing was inhibited by morphometric features. The reported median chloride and calcium and concentrations of six acid-sensitive lakes located in the southwest of the province were 2.5 and 3.7 mg/L, respectively (Phippen *et al.*, 1996; Jeffries, 1997).

The impact of road salts on water quality was monitored for the Serpentine River in British Columbia's Lower Fraser Valley. Electronic data recorders monitored water temperature, pH, water level and conductivity every 15 minutes. Peaks in conductivity were observed during thaw periods, following a cold period when roads were sanded and salted (Whitfield and Wade, 1992). Furthermore, periods of elevated conductivity were followed by increased water levels which are characteristic of snow melt. Results of this study indicate that organisms living in certain streams during winter months may be subject to fluctuations in salt concentrations.

#### 2.6.2.5 Yukon, Northwest Territories and Nunavut

Few data were identified from the Yukon, Northwest Territories and Nunavut.

### *2.6.3 Environmental concentrations: Benthic sediments*

Because inorganic salts used for road maintenance are highly soluble and interactions with sediment particulates is minimal, they are expected to accumulate in sediment porewater rather than in the solid phase. The recent study (Mayer *et al.*, 1999) of an urban pond (Rouge River Pond) shows that the sediment porewater which is in a steady state with the overlying water, enriched in inorganic salts, may itself attain high salt concentrations. High concentrations of salts

in sediment porewater not only have osmotic and a direct toxic effect on the benthic biota, but through complexation with chloride, they also augment the concentrations of dissolved heavy metals (e.g., cadmium), which are available and toxic to benthic organisms.

### *2.6.4 Environmental concentrations: Wetlands*

Wetlands are an important landscape feature in Canada. Their most distinguishing features are presence of standing water, unique wetland soils, and vegetation adapted to or tolerant of saturated soils (Mitsch and Gosselink, 1986). Canada has a great variety of wetlands; detailed descriptions of various types of wetlands can be found in Mitsch and Gosselink (1986).

There is only limited information on the chemical characteristics of coastal and inland freshwater wetlands with respect to chloride, for much of the work on wetlands is concerned with nutrient cycling, acidification and with geochemistry of metals. A 1987 study of wetlands within the Kejimkujik National Park (Wood and Rubec, 1989) assessed the chemical characteristics of wetlands. The authors reported significant differences in peat chemistry between the bogs and fens, in particular in sodium and calcium concentrations. The concentrations of calcium, sodium and chloride in peat from bogs were 0.17, 0.8 and 0.15 mg/L, respectively. The concentrations of calcium, sodium and chloride in peat from fens were 0.32, 1.5 and 0.12 mg/L. There was no difference in the surface water chemistry between bog and fen. The concentrations of calcium, sodium and chloride in water of bogs were $6x10^{-4}$, $3.0x10^{-3}$ and $3.5x10^{-3}$ mg/L, respectively, and the concentrations of calcium, sodium and chloride in water of fens were $6x10^{-4}$, $2.8x10^{-3}$ and $3.9x10^{-3}$ mg/L, respectively.

Bourbonniere (unpublished data) investigated geochemistry of wetlands in Nova Scotia and Ontario. He measured the major ion chemistry in porewater of the ombrotrophic bog in Barrington County in Nova Scotia. The measured concentrations (in mg/L) were 9.6 to 24 for chloride, 5.2 to 2.8 for sodium and 0.47 to 1.5 for calcium. The concentrations of calcium, sodium and chlorine in Beverly Swamp, Ontario, were 58.1 to 95.3, 5.1 to 20.0 mg/L and 8.7 to 41.2 mg/L, respectively. The water composition of potholes described in the previous section may be considered to be characteristic of the prairie wetlands. No studies were found that address the impact of road salt application on the chemistry of wetlands. Two studies were presented in the patrol yard section that focus on the impact of salt depots on wetlands.

### *2.6.5 Environmental concentrations: Urban lakes and ponds*

Small urban lakes and ponds which receive road runoff are susceptible to changes in ion concentrations. There are only limited data on the chloride concentrations in such bodies. In the absence of such data, ponds that are part of an urban stormwater management system can be used as a reasonable surrogate. Numerous ponds have been constructed and remain a widely used form of watershed management in urban areas. Although these ponds are engineered water bodies designed primarily for hydraulic flow management and stormwater treatment, they

have developed aquatic ecology similar to natural small urban ponds. Like natural urban aquatic systems, these ponds are wetland habitats for many species of flora and fauna. They are likely candidates for showing maximum chloride concentrations, since they represent the type of water body that receives the maximum exposure to chloride loadings from winter maintenance activities.

A study of Lake Wabukayne (Free and Mulamoottil, 1983), a small human-made lake in Mississauga, Ontario, reported high chloride concentrations (200–2000 mg/L Cl) and temporary meromixis during the winter and early spring. Chloride concentrations of 1100 to 2000 mg/L (S. Vickers, personal communication) were measured in the Harding Pond in Richmond Hill in the GTA. Seasonal surveys of the stormwater retention ponds in the GTA (Mayer *et al.*, 1996; Mayer, unpublished data) showed high concentrations of chloride during the winter months. Chloride concentrations of 380 and 800 mg/L, respectively, were measured in the Heritage and Unionville ponds, which are situated in residential settings (Mayer, unpublished data), while chloride concentrations as high as 5910 mg/L were measured in the Col. S. Smith Reservoir, receiving runoff from a multi-lane highway (Queen Elizabeth Way) in February of 1999.

Both a mass balance and a sediment study were performed on the Rouge River Pond, situated in the Rouge River Valley, Scarborough, Ontario, near Highway 401 and Port Union Road. The mass balance study was conducted to measure the pollutant removal and the dynamics of several water quality constituents between 1995 and 1998 (Liang, 1998). The initial studies during 1995, 1996 and 1997 focussed on balances during the ice-free season. A chloride imbalance related to permanent meromictic conditions in the pond was shown, with meromixis likely due to combination of the pond design and high road salt loadings. The salt concentrations calculated as sodium chloride in the bottom layer of the pond was of the order of 5000 mg/L. Elevated concentrations of metals and ammonia were also measured in this bottom layer. The sediment study (Mayer *et al.*, 1999) investigated chemistry and toxicity of sediment porewater and assessed the solid phase metal chemistry. A geochemical model was formulated to assess the impact of salts on metal speciation. The investigation revealed that sediment porewater which is in the steady state with the overlying water, enriched in inorganic salts, may itself attain high salt concentrations. At the sediment-water interface, concentrations of chloride and sodium greater than 3000 mg/L and 2000 mg/L, respectively, were measured in the porewater. A gradual decrease with depth in sediment was observed for both ions; however, even at a depth of 40 cm below sediment–water interface, the chloride concentrations were about 1500 mg/L.

### *2.6.6 Spatial analysis of chloride from road salts in Canadian watersheds*

This section presents a spatial overview of chloride concentrations by watershed in Canada. Estimated chloride concentrations from loadings by sodium chloride road salts were also compared to chloride concentrations observed at water quality monitoring stations.

#### 2.6.6.1 Watersheds

A sub-basin watershed coverage was selected for this analysis. This level watershed was selected because it was most compatible with data on road salt loadings. Estimates of runoff were made for each watershed (Figure 11). Watersheds in the Prairie Provinces have the least runoff per unit area, while watersheds west of the Rockies and in the Maritime Provinces have the greatest volume of runoff.

Road salt loadings were estimated using data provided by Morin and Perchanok (1999). Figure 12 depicts chloride loadings from road salts per unit area watershed. Watersheds in southern Ontario, southern Quebec and the Maritimes have the highest loadings. Within these areas, higher loadings are in the most urbanized watersheds. The Island of Montréal has the highest loading per unit area (250 g/m$^2$ of Cl).

#### 2.6.6.2 Spatial exposure to road salt in Canadian watersheds

Data on runoff and road salt loadings were combined to estimate chloride concentrations related to road salts (Figure 13). Results indicate that the Island of Montréal has potentially the highest concentration of chloride from road salts in runoff. Figure 13 also indicates that watersheds on the north shore of Lake Ontario, notably those largely influenced by municipalities in the GTA, also have high road salt chloride concentrations.

#### 2.6.6.3 Comparison of spatial variation to observed surface water chloride values

Observed chloride concentrations in Canadian watersheds are provided in Figure 14. The concentrations of chloride in surface water are based on mean values obtained from federal and provincial water quality monitoring stations in Canada. This map indicates that watersheds in the Prairie Provinces are those with the highest concentrations. These concentrations can be attributed to saline lakes and rivers situated in this part of the country. Watersheds near urban areas also have higher chloride concentrations.

Figure 15 shows the portion of observed chloride concentrations in Canadian watersheds that could be attributed to road salt. This compares concentrations of chloride from road salt to those observed at the mouths of rivers from all natural and anthropogenic sources. In most of Canada, the portion of chloride from road salt application is 40% or less (based on the categories presented in Figure 15). However, for some watersheds, particularly those in the most urbanized areas of Canada, the ratio is greater than 1. While it is obvious that chloride derived from road salts cannot exceed 100% of the observed chloride concentrations, it must be remembered that all values are based on annual means. Spatial and temporal sampling may under-represent pulsed, localized entry of salts, notably in urban areas where flow may be channelled through storm sewers or other managed drainage systems. In addition, all chloride from road salts may not be flushed on an annual basis and may be stored in soils and groundwater.

Results indicate that watersheds in urban areas, particularly those in southern Ontario, southern Quebec, the Maritime Provinces and larger urban centres in the Prairie Provinces, have the highest concentrations of chloride in runoff. By calculating the ratio between observed and estimated concentrations, it was possible to identify watersheds that face the greatest risk of adverse effects from the use of road salts.

### *2.6.7 Summary and conclusions*

Because of the conservative nature of chloride in aquatic ecosystems and its common presence in all commercially used road salts, chloride is the best surrogate measure of salt concentrations in surface waters, where impacts of road salts are investigated. Furthermore, chloride is one of the chemical parameters most commonly reported by various monitoring agencies. Hence, chloride concentrations in surface waters are important for the assessment of environmental impacts of road salts.

The data compiled in this report show a broad range of background chloride concentrations in Canadian surface waters. The differences stem from the variance in bedrock and surficial geology, climate and the proximity to the sea. Anthropogenic impacts are also evident from the data. The data indicate that the water bodies most sensitive to the impacts of road salts applied to roadways are small ponds and streams draining large urbanized areas, as well as streams or lakes draining major roadways.

The spatial analysis of chloride concentrations in Canadian watersheds, presented here, identifies watersheds in Canada that face the greatest risk of adverse effects from the use of road salts and needing more detailed consideration.

## 3.0 SUMMARY OF CRITICAL INFORMATION AND PROPOSED ASSESSMENT OF "TOXIC" UNDER CEPA 1999

### 3.1 CEPA 64 1999(a): Environment and CEPA 1999 64(b): Environment on which life depends

#### *3.1.1 Assessment approaches*

CEPA 1999 defines "environment" quite broadly, to include all biotic and abiotic components of the biosphere (CEPA 1999 Section 3); it does not distinguish between "natural" and "non-natural" environments. Indeed, all ecosystems can be considered to have been subjected to stress or modifications by human activity, be it at a local (e.g., habitat destruction, emission of pollutants in liquid effluent), regional (e.g., dispersion of atmospheric pollutants) or global scale (e.g., persistent organic pollutants [POPs], global atmospheric effects). Modified environments are critical to the survival of many individuals and populations. In areas heavily impacted by urbanization, industrialization or agriculture, modified landscapes such as rights of ways or impoundments can in fact offer the only habitats available for many species locally or regionally. The assessment of priority substances therefore does not distinguish between effects on natural and modified environments.

The approach for the environmental assessment of PSL substances involves characterizing entry, exposure and effects of a substance, which ultimately permits the characterization of the risks posed by the substance (Environment Canada, 1997). This may involve the use of both laboratory and field-derived data. Empirical field evidence linking environmental changes to entry of the substance can provide strong indications of actual risks.

It can be assumed that all road salts eventually enter the environment, whether from losses from storage or patrol yards, from roadway application, or from disposal of waste snow. Although all chloride ions will ultimately be found in surface waters, ions from inorganic chloride road salts and ferrocyanides will be released to or move through soil, groundwater, surface water and air, and organisms can be exposed to road salts through all these media. Therefore, all environmental compartments are of concern for the assessments of road salts. Environmental effects can be either biotic or abiotic. Thus, endpoints of concern can include effects on individual organisms, populations or communities, as well as abiotic endpoints such as deterioration of soil structure or lake stratification which disrupts seasonal mixing of waters.

While there has not been systematic assessment of exposure to road salts for any given compartment across Canada that would permit detailed quantitative risk characterization at the national scale, many individual studies are available that permit the establishment of clear relationships between the use of road salts and their impacts on biotic and abiotic systems.

The following sections will characterize the risks associated with releases of road salts into the environment, by reviewing the entry, exposure and effects related to five environmental

compartments or biotic groups with regards to inorganic chloride salts. Data pertinent to ferrocyanides and their environmental risks are reviewed in a separate section.

## 3.2 Groundwater

### *3.2.1 Introduction*

This section provides an overview of the road salt impacts to groundwater, and ultimately surface water quality, and is a summary of a report prepared by Johnston *et al.* (2000). Discussion focusses on the fate and impact of sodium chloride. Morin (2000) presented a discussion of case histories of the impacts to groundwater and surface water quality associated with salt storage areas.

Data on concentrations in groundwater are frequently discussed in published and unpublished literature in terms of exceedences of drinking water quality guidelines. These guidelines are set on the basis of taste thresholds at 200 mg/L $Na^+$ and 250 mg/L $Cl^-$ (CCME, 1998). Although the use of groundwater as a drinking water resource is not considered as part of this assessment, review of reported exceedences of a concentration of chloride of 250 mg/L is pertinent to the assessment of potential impacts on aquatic biota. As reviewed in Section 2.3, the No-Observed-Effect Concentration (NOEC) for the 33-day survival of early life stage fathead minnow was 252 mg/L chloride, while lethality data modelled for chronic exposure indicated that 10% of aquatic species would be affected at chloride concentrations of about 240 mg/L.

### *3.2.2 Groundwater principles*

#### 3.2.2.1 Hydrologic cycle

The degree to which road salts may impact the groundwater environment will vary significantly, depending on the road salt loading, climatic conditions, surface and subsurface soil conditions, and location of the site within the overall hydrogeological environment.

Precipitation that falls across an area, as rain or snow, contributes to a number of hydrologic processes. A portion of the precipitation will run off as overland flow from impervious surfaces, such as roadways and parking lots, and is eventually directed by open ditches or subsurface piped systems that discharge to streams, wetlands, lakes or other surfaces, water features. Overland flow will result in the direct migration of surficial contaminants, like road salts, to surface water features, typically in the time frame of hours.

In certain settings, a portion of precipitation will infiltrate the shallow soil zone and move laterally through the unsaturated zone above the water table as interflow to the local discharge

area. The transport of contaminants to surface water features as interflow typically occurs in the time frame of hours to days.

The balance of precipitation is subject to evapotranspiration or infiltrates as groundwater recharge to the water table. Contaminants introduced to the local, intermediate, or regional groundwater flow systems may take several years to several hundred years before discharging as baseflow to surface water features.

#### 3.2.2.2 Unsaturated flow and groundwater recharge

The amount of precipitation that infiltrates to the water table depends on a number of factors, including the duration and intensity of the rainfall event, the initial soil moisture content and the soil moisture characteristics. Based on the general temperature and precipitation pattern in Canada, the majority of groundwater recharge in a year is expected to occur in the late winter and early spring, as a result of winter snow melt and spring rains (Geber and Howard, 1997; Singer *et al.*, 1997).

To provide an indication of travel times, vertical travel times through the unsaturated zone may be expected to range from less than 0.5 m/yr to greater than 20 m/yr. In areas with thick unsaturated zones (i.e., 20–30 m), travel times for infiltrating precipitation to reach the water table may be in the range of 5 to 20 years in sandy soils. These travel times are important when considering the impacts to downgradient receptors and the time required before remedial measures implemented at the source would have noticeable effects.

#### 3.2.2.3 Saturated flow and contaminant migration

Once below the water table, the movement of water is controlled by the fluid potential and the permeability of the geologic material. When evaluating the migration of solutes, like $Na^+$, $Ca^{2+}$ and $Cl^-$ within groundwater environments, several other physical and chemical processes must be considered. Mechanical dispersion, molecular diffusion and density effects represent the primary physical transport mechanisms that affect the migration of $Na^+$, $Ca^{2+}$ and $Cl^-$.

### *3.2.3 Impacts of road salts on groundwater quality*

#### 3.2.3.1 Factors controlling the migration of road salts

One of the primary concerns associated with sodium chloride road salt is its high solubility in water. Once dissolved, $Na^+$ and $Cl^-$ will migrate with infiltrating precipitation to the water table. The migration rate of $Cl^-$ will be the same as that of the water. This is not the case for $Na^+$, which can be affected by cation exchange reactions in certain geologic environments. The following equation presents the ion exchange reaction for $Na^+$.

$$2Na^{+} + Ca_{(adsorbed)} \leftrightarrow Ca^{2+} + 2Na_{(adsorbed)}$$

In the equation, $Na^{+}$ is exchanged with Ca adsorbed to clay-rich materials. The net effect of this reaction is a decrease in $Na^{+}$ concentrations within the infiltrating groundwater and a Na:Cl ratio of less than 1. Reduced $Na^{+}$ concentrations in groundwater impacted by road salts have been documented by Howard and Beck (1993) and Pilon and Howard (1986).

3.2.3.2 Predicted road salt concentrations in groundwater

To provide an understanding of the impact that road salting may have on groundwater quality, an estimate of the amount of road salt available for dissolution in infiltrating precipitation is required. A simple spreadsheet mass balance model was developed to provide an indication of the equilibrium Cl concentration in shallow groundwater (Johnston *et al.*, 2000). The spreadsheet model is based on the dissolution of the total Cl retained within the soil by recharging precipitation, and does not consider any additional Cl from other sources. The calculated Cl concentrations can therefore be considered representative of regional scale equilibrium Cl concentrations downgradient of a saltable road network. It should be noted that the model does not provide an indication of potential Cl concentrations immediately downgradient of a source area, such as an individual roadway, and, as a result, higher Cl concentrations may be expected in such areas.

Input to the model includes groundwater recharge rates, road salt application rates and road densities. Recharge rates ranging from 5 to 40 cm/yr were selected based on a range of soil types. The Cl application rates were based on typical road salt application rates for both provincial and municipal road networks as discussed in Section 1.2 (Road salts loadings). The road salt available for infiltration to the water table was estimated based on the ranges reported by Wulkowicz and Saleem (1974), Scott (1980) and Howard and Haynes (1993). Road densities in the range of 1 to 15 2-lane-km/km$^2$ were selected based on the data presented in Morin and Perchanok (2000) and Stantec (unpublished data). Road densities of 0.01 to 0.1 2-lane-km/km$^2$ were assumed to be characteristic of low-density rural land use, 1 to 5 2-lane-km/km$^2$ were assumed to be characteristic of medium-density rural to semi-rural land use, and 10 to 15 2-lane-km/km$^2$ were assumed to be characteristic of urban land use.

Johnston *et al.* (2000) presented the predicted Cl concentrations for soils with groundwater recharge rates ranging from 10 to 40 cm/yr. As expected, Cl concentrations for a given recharge rate increase with increased loading and display the highest concentrations for the highest road density and highest percentage Cl retained. Chloride concentrations decrease with increasing recharge rates due to the dilution effects of increased recharge. The highest Cl concentration, 3600 mg/L, was predicted for soil with a recharge rate of 10 cm/yr, a loading of 40 tonnes-Cl/2-lane-km, and 60% of the Cl applied available for dilution in recharging precipitation. For comparison, the Cl concentration for the same loading and percentage retained is 900 mg/L for soils with a recharge rate of 40 cm/yr. It is expected that the

percentage of Cl retained will vary significantly between a site with a recharge rate of 10 cm/yr versus 40 cm/yr. This is due to the fact that runoff would be higher for the site with a recharge rate of 10 cm/yr, and therefore less Cl should be retained for dissolution in infiltrating precipitation.

Figures 16 to 18 present regional scale groundwater Cl concentrations that were predicted for various road salt application rates, road densities and recharge rates. In each Figure, an envelope corresponding to the maximum and minimum Cl concentrations is presented. Average Cl concentration envelops for medium- and high-density road networks are also presented, assuming the average percentage Cl retained of 30% and 40%.

For soils with recharge rates of 10 cm/yr, typical of clay-rich soils, Cl concentrations may exceed 250 mg/L for Cl application rates of approximately 5 tonnes-Cl/2-lane-km under high-density road networks (Figure 16). Under medium road densities, Cl concentrations are predicted to remain below 250mg/L for road salt applications rates of approximately 10 to 15 tonnes-Cl/2-lane-km. For low-density road networks, typical of a rural setting, regional scale chloride concentrations are predicted to remain well below 250 mg/L.

Figure 17 presents the estimated groundwater concentrations for a soil with a recharge rate of 20 cm/yr, typical of sand. Due to dilution from the increased recharge, slightly higher Cl application rates can be supported before a concentration of 250 mg/L is exceeded. Under high- and medium-density road networks, Cl application rates above 11 tonnes-Cl/2-lane-km and 32 tonnes-Cl/2-lane-km, respectively, may result in regional-scale Cl concentrations above 250 mg/L.

At recharge rates typical of very permeable soils, such as gravels or fractured rock, groundwater Cl concentrations only exceed 250 mg/L for high-density road networks. In this case, Cl application rates above 22 tonnes-Cl/2-lane-km are predicted to result in concentrations above 250 mg/L (Figure 18).

The mass balance modelling completed for this section indicates that road salt application rates above approximately 15 tonnes-Cl/2-lane-km, or 24 tonnes-NaCl/2-lane-km, will result in regional scale groundwater concentrations greater than 250 mg/L in any soil condition under high-density land uses. Considering road salt application rates in southern Ontario, southern Quebec and the Maritime Provinces are in the range of 20 to 50 tonnes-NaCl/2-lane-km, highly developed urban areas in these provinces are at the greatest risk of wide-scale groundwater impacts associated from road salting. In addition to groundwater impacts, surface water quality within these areas of Canada will be subject to the discharge of groundwater with elevated $Na^+$ and Cl concentrations as baseflow, particularly during the late summer and fall.

The mass balance modelling indicates that under low-density land use, Cl concentrations will remain well below 250 mg/L, reaching a maximum concentration of 24 mg/L

for road salt application rates of 40 tonnes-NaCl/2-lane-km. It should be noted, however, that this concentration represents an average regional concentration and higher concentration may be expected immediately downgradient from point sources associated with individual roadways.

3.2.3.3 Plume migration and impact assessment

The above section provides an overview of the wide-scale impact associated with non-point source loading from road salting in rural and urban areas. The impact on groundwater quality and plume development from point source loading associated with road salting along an individual roadway is discussed below.

To provide an indication of maximum Cl concentrations and the effects of dispersion on plume concentrations, a numerical solute transport model was developed for a simple unconfined sand aquifer system using the finite difference modelling codes MODFLOW (McDonald and Harbaugh, 1988) and MT3D (Zheng, 1990). The simplified aquifer was assigned a lateral hydraulic conductivity of $1x10^{-4}$ m/s, vertical hydraulic conductivity of $1x10^{-5}$ m/s, specific yield of 0.25, effective porosity of 0.30, longitudinal dispersivity of 10 m, and lateral and vertical transverse dispersitivies of 1 m and 0.1 m, respectively. Linear constant-head boundaries were assigned at the upgradient (17.5 m) and downgradient (15 m) extents of the model to simulate a lateral hydraulic gradient of 0.005 m/m across the 500-m model length. Recharge was assigned at 30 cm/yr to the entire model domain.

Within the simulated steady-state flow field, a square constant concentration source term of 1000 mg/L was assigned at the water table to represent the Cl loading from a section of roadway. This concentration is within the range (323–2930 mg/L, average 923 mg/L) for shallow groundwater beneath a four-lane arterial road in Kitchener, Ontario (Stantec, unpublished data). The formation and migration of an unretarded, dissolved-phase Cl plume was simulated for 5000 days, followed by the dissipation of the plume after removing the concentration source term.

At a simulated time of 100 days, typical of early summer following recharge of groundwater with elevated Cl concentrations from winter road salting, groundwater concentrations parallel to the plume showed the formation of a typical "cigar-shaped" plume as defined by the 10 mg/L contour. At 100 days, the 10 mg/L contour has migrated approximately 40 m downgradient from the source area with the 250 mg/L contour restricted to within approximately 10 m of the source area. After a period of approximately five years, the plume has reached a steady-state condition as defined by the 10 mg/L contour in which the flux from the source area is balanced by the flux across the plume boundary. The 10 mg/L contour under steady-state conditions is located approximately 200 m downgradient from the source, while the 250 mg/L contour moved 20 m downgradient from the source area.

After a simulation period of approximately five years, the Cl source was removed to provide an indication of the time required for concentrations to dissipate. Chloride

concentrations decreased rapidly after 50 days with no simulated concentrations above 250 mg/L.

The above simulations indicate that impacts associated with road salting along individual highways may be limited in extent due to groundwater flow and transport processes, depending on the aquifer properties. Based on the modelling results, shallow wells and surface water features located within 20 m of salted roads are at the greatest risk to Cl impacts. The modelling does suggest that if road salting activities are discontinued, Cl concentrations within the shallow aquifer may improve significantly over time frames of several months to years.

### *3.2.4 Case studies*

This section presents modelling and field measurements for specific areas in Canada. Additional case studies involving impacts to groundwater quality associated with roadways and maintenance salt storage yards are presented in Morin (2000).

One method for assessing the regional-scale impacts associated with road salting was that applied by Howard and Haynes (1993) in the Highland Creek catchment located near Toronto, Ontario. Through detailed measurements of stream flow and Cl concentrations over a three-year period, it was estimated that only 45% of the Cl applied as road salt within the basin was removed by surface water runoff. The remaining 55% was interpreted to be stored within the groundwater system. At current salt application rates, Howard and Haynes (1993) estimated an average Cl concentration of 426 +/-50 mg/L in groundwater discharging as baseflow to Highland Creek. While road salt application rates were not presented, the total loading over the basin was approximately 200 g-NaCl/m$^2$. Assuming a road density typical of an urban environment, the road salt application rate over the study area is estimated to be in the range of 20 to 30 tonnes-NaCl/2-lane-km, which is similar to that predicted based on the mass balance modelling completed as part of this report.

Further evidence of the impact on groundwater quality and discharge to surface water features due to road salting in urban areas is presented in Howard and Beck (1993) and Eyles and Howard (1988). Chloride concentrations in springs discharging to Lake Ontario, along the Scarborough Bluffs near Toronto, were measured and found to contain Cl concentrations of approximately 400 mg/L. The concentrations measured by Howard and Beck (1993) and Eyles and Howard (1987) were similar to that estimated by Howard and Haynes (1993) for the Highland Creek watershed.

Long-term Cl concentrations from municipal supply wells provide further evidence of impacts to groundwater quality associated with winter road salting. Figure 19 presents Cl concentrations from municipal water supply wells in an urban centre of southern Ontario. Data on current Cl application rates in the study area near the wells indicate that application rates have ranged from 18 to 36 tonnes-NaCl/2-lane-km, with an average application rate of 28

tonnes-NaCl/2-lane-km. Chloride concentrations beginning in the early 1960s were less than 50 mg/L and have increased steadily to concentrations of 250 to 300 mg/L in the late 1990s (Figure 19). One of the key issues with respect to the trends indicated in Figure 19 is that Cl concentrations are continuing to rise and have not reached equilibrium concentrations. The time to steady state (the time when salt inputs are balanced by salt output) depends on local hydrogeological conditions and the size of the catchment area (Howard *et al.*, 1993). Howard *et al.* (1993) used two numerical models to demonstrate temporal and spatial changes in water quality. The model "FLOWPATH" showed that chemically conservative contaminants such as chloride released within a few kilometres of rivers and Lake Ontario will discharge in about five years. Contaminants that are released in more central areas will take more than 100 years to be flushed from the groundwater system. When road salt is evenly distributed in a representative 460 $km^2$ region of the GTA, Howard *et al.* (1993) demonstrated, using the FLOWPATH model, that the average chloride concentrations will reach steady-state value within 200 years of initial salt application. Using another model, AQUA, in a smaller area near Toronto, steady state was reached in just 30 years. At steady state, the levels of chloride at a distance of 200 m from the salted highways are two to three times the levels of chlorides observed in the discharging base flow.

Williams *et al.* (1997) investigated chloride concentrations in 20 springs in southeastern Ontario. Chloride concentrations ranged from 8.1 mg/L to 1149 mg/L. The higher chloride concentrations originated from groundwater that may be contaminated by road salt. Williams *et al.* (1999) continued this research, noting that the mean chloride concentration at the Glen Majors Conservation Area was 2.1 mg/L and about 100 mg/L in rural areas. Chloride concentrations in springs near urban areas were higher (>200 mg/L) with the maximum concentration 1345 mg/L and mean 1092 mg/L. This spring was adjacent to a highway and bridge. Chloride concentrations at these urban sites also increased between November 1996 and November 1997. Salinity contamination was related to road salt. Williams *et al.* (1999) noted that spatial patterns in road salt contamination were more readily detected by sampling springs than creeks because chloride concentrations in spring waters (i.e., discharging groundwater) exhibited relatively little seasonal variability. In contrast, chloride concentrations in creeks were highly variable seasonally.

Howard and Taylor (1998) reported high concentrations of chloride in springs discharging from aquifers along the Scarborough Bluffs, a stretch of Lake Ontario shoreline east of Toronto, and along an urban–rural transect from the Oak Ridges Moraine to Metropolitan Toronto. Concentrations of 2800 mg/L chloride were detected in springs issuing from shallow aquifers in the Oak Ridges Moraine–Toronto area. The primary source of the chloride contamination is road de-icing chemicals (Howard and Beck, 1993).

In 1970, Autoroute 55 was constructed between 50 and 200 m from wells used by Trois-Rivières-Ouest to obtain groundwater. By 1976, after the autoroute had been open for a few years, an increase in salinity was noted (Gélinas and Locat, 1988). In the early 1980s, a plume of salty groundwater was identified. Chloride concentrations in samples from piezometers

ranged between 3 and 1500 mg/L. Data collected in 1985 revealed that the shape and extent of the plume varied depending on the time of year, and the quantity of water pumped from each of the six municipal pumping stations. Data for 1985–86 indicate that concentrations gradually increase throughout the spring (during snow melt) to peak in August and September. Higher concentrations were observed for a municipal pumping station located downgradient from the highway. Concentrations at most wells upgradient from the highway were less than 5 mg/L. Mean chloride concentrations in one station downgradient (80 mg/L) were about 6 times higher than the average concentration in a nearby station upgradient (14 mg/L).

The municipality of Cap-de-la-Madeleine pumps water from 27 wells. While the quality of this water was considered to be extremely good, certain wells have experienced a gradual increase in the concentration of chloride since the 1970s that is attributed to the use of de-icing road salts (Delisle amd Dériger, 2000). Overall, wells located downgradient from major roadways are most susceptible to contamination from the use of road salt. Delisle (1999) further confirmed that some ditches are not connected to a drainage system; in these areas, runoff is left to percolate through the soils.

### *3.2.5 Conclusions*

The potential for impacts to groundwater and surface water quality were evaluated using a mass balance technique which provides an indication of potential regional scale $Cl^-$ concentrations downgradient of saltable road networks. The mass balance modelling indicates that for road salt application rates above 20 tonnes-NaCl/2-lane-km, regional scale groundwater $Cl^-$ concentrations greater than 250 mg/L will likely result under high-density road networks, typical of urban areas. Considering road salt application rates throughout Canada, urban areas in southern Ontario, southern Quebec and the Maritime Provinces are at the greatest risk to wide-scale groundwater impacts associated with road salting. The mass balance modelling completed as part of this report indicates that rural and semi-rural areas are not as likely to be impacted by $Cl^-$ concentrations above 250 mg/L on a regional scale. However, local impacts are expected along individual roadways and have been documented in numerous studies.

Studies show that at present levels of salt application, only 45% of the salt applied is flushed into surface waters every year. The remaining 55% enters shallow subsurface waters and once steady-state concentrations are attained (200 years in the Toronto area), >400 mg/L chloride may be discharging from groundwaters into surface waters.

Groundwater containing road salts will eventually upwell into the surface water or emerge as springs. Research has shown that only a portion of the road salts that are applied to roads are removed by surface water runoff and a significant proportion of the salt may be stored within the groundwater system. Elevated concentrations of chlorides have been detected in both groundwater and in groundwater that has emerged to the surface as springs. Predicted and measured concentrations in groundwaters and springs exceed those identified as lethality

thresholds for many organisms, as identified in Section 2.3, where 10% of species can be expected to be affected by concentrations greater than 240 mg/L and population shifts may occur at even lower concentrations.

### 3.3 Surface water ecosystems

Evans and Frick (2000) have conducted an extensive review and analysis of literature pertinent to the assessment of effects of inorganic chloride salts on aquatic biota. This included in-depth examination and presentation of salinity in the environment; natural factors affecting water salinity and the entry of road salts into the environment; literature review of the effects of road salt applications on the salinity of aquatic ecosystems and on lake meromixis; the lethal and sub-lethal effect levels of sodium chloride and other chloride salts as determined from laboratory studies, including factors affecting toxicity and limitations of these studies; the effects of natural forms of salinity on aquatic environments; the impacts of road salts on stream, lake and wetland ecosystems; and Tiers 1, 2 and 3 characterization of risks.

Some of the key assessment findings are presented below, with regards to the nature of potential impacts and the likelihood and magnitude of adverse effects occurring in aquatic ecosystems as a result of release of road salts to the environment. As provided for in CEPA 1999 section 76.1, a weight of evidence approach and the precautionary principle are to be applied when assessing whether a substance is toxic or capable of becoming toxic. As noted in Environment Canada (1997), the use of several lines of evidence can strengthen confidence in assessment conclusions. Field evidence can be important in characterizing risk. The assessment of impacts on aquatic ecosystems is based on a number of approaches.

**1. Toxicity thresholds and quotient-based risk characterization:** A quotient-based approach is used to determine the likelihood and magnitude of adverse effects occurring in aquatic ecosystems as a result of release of road salts into the environment. This approach is based on comparisons of concentrations of chloride in the aquatic environment resulting from the release of road salts (based on literature and analyses done for this assessment) and toxicity thresholds for chloride salts as identified in laboratory studies.

**2. Field evidence of population or ecosystem effects:** While the quotient-based approach generally focusses on consideration of toxicity thresholds, community structure can be affected by environmental conditions which, while not necessarily exposing organisms to concentrations that are of themselves toxic, will result in selective advantage for certain populations or species and thereby result in shifts in populations and changes in community structure.

**3. Abiotic effects:** Through their interactions with physical, chemical or biological components of the environment, substances may alter the abiotic environment and thereby affect ecosystems.

### *3.3.1 Quotient-based risk characterization*

The quotient-based environmental risk assessment is based on the procedures outlined in Environment Canada (1997). Based on possible exposure scenarios, a hyperconservative or conservative Estimated Exposure Value (EEV) is selected; an Estimated-No-Effects Value (ENEV) is determined by dividing an experimental Critical Toxicity Value (CTV) by an application factor to account for uncertainty surrounding the extrapolation to chronic or pulsed exposure, extrapolation from laboratory to field conditions, and interspecies and intraspecies variations in sensitivity. The CTV can be based on a wide range of toxicity responses, including mortality, growth, reproduction, fecundity, longevity, diversity, productivity, community structure and diversity. A hyperconservative (Tier 1) or conservative (Tier 2) quotient (EEV/ENEV) is calculated for each pertinent sensitive taxon in order to determine whether there is potential environmental risk in Canada. If these quotients are less than 1, it can be concluded that the substance poses no significant risk to the environment and the risk assessment is completed. If, however, the quotient is greater than 1 for a particular assessment endpoint, then the risk assessment for that endpoint proceeds to a Tier 3 analysis where more realistic assumptions are used and the likelihood and magnitude of effects are considered. This latter approach involves a more thorough consideration of sources of variability and uncertainty in the risk analysis.

#### 3.3.1.1 Tier 1 and Tier 2 assessments

*Estimated Exposure Value (EEV)*

A Tier 1 assessment is based on a hyperconservative exposure scenario, generally assuming that the EEV is the maximum concentration measured or likely to be encountered in the Canadian environment. The highest reported sodium chloride concentrations in the aquatic environment have been associated with highway runoff, road salt–contaminated snow, and with contaminated waters near salt storage depots.

In Ontario, chloride concentrations as high as 19 135 mg/L have been reported in highway runoff from the Skyway Bridge (Mayer*et al.*, 1998). Delisle *et al.* (1995) reported that chloride in snow carried by Montréal trucks occurred in an average concentration of 3851 mg/L, with a maximum reported concentration of 10 000 mg/L. Mayer *et al.* (1999) reported chloride concentrations high as 89 000 mg/L in meltwater from some city streets. In Maine, chloride concentrations in surface waters of four wetlands located within 30 m of salt storage depots reached concentrations of 13 500 mg/L; concentrations remained elevated throughout the March to October sampling period (Ohno, 1990). Therefore, for the purposes of Tier 1 assessments, an EEV of 10 000 mg/L was used to represent estimated maximum chloride concentrations in snow-melt draining from highways into small receiving water bodies such as ditches and creeks. Such a concentration also approximates those observed in wetlands near road salt storage depots.

Tier 2 assessments involve a further analysis of exposure and/or effects to calculate a quotient that is still conservative, but more "realistic" than the hyperconservative quotient calculated in Tier 1 (Environment Canada, 1997). Road salt has been shown to have its greatest impact on the chloride levels in urban creeks and rivers. In Canada, the best documented impacts of road salt on chloride levels in aquatic systems have been for the Toronto area. Hence, this data set was examined to find a more realistic estimate of the Tier 2 EEV.

Chloride concentrations were measured in several streams in the Toronto Remedial Action Watershed over 1990–96 (see Evans and Frick, 2000). Data were collected seasonally. Most stations were sampled fewer than 50 times during the multi-year study. Minimum chloride concentrations ranged from 1 to 51 mg/L chloride while maximum concentrations were considerably higher. Maximum chloride concentrations reported at individual stations included 2140 to 3780 mg/L at three stations on Etobicoke Creek; 3470 mg/L at Mimico Creek; 4310 mg/L at Black Creek; 96 to 4310 mg/L at five stations on the Humber River; 960 to 2610 mg/L at three stations on the Don River; and 1390 mg/L at Highland Creek. Seasonal plots of chloride variations in Highland Creek over 1990–93 show several winter sampling periods in which chloride concentrations exceeded 1000 mg/L. Williams *et al.* (1999) reported that an Ontario spring located near a highway and bridge had a mean chloride concentration of 1092 mg/L as a probable result of road salt contamination of groundwater. While the maximum chloride value observed in creeks and rivers in the Toronto area which have been contaminated by road salt is in the range of 2000 to 4000 mg/L, the frequency and duration of such occurrences is likely variable. Therefore, a less conservative estimate of 1000 mg/L was used as the EEV in the Tier 2 assessments. Chloride concentrations in this range have been commonly observed in Toronto area creeks and rivers, in a contaminated spring in the Toronto area, and in a bog contaminated by a salt storage depot (Wilcox, 1982).

*Critical Toxicity Values*

While a number of field studies have demonstrated impacts of salinity on diversity, standing stocks, behaviour and survivorship (Evans and Frick, 2000), these studies generally do not allow establishment of clear effects thresholds. Therefore, only laboratory data are used in the tiered assessments. Assessments are performed for all major components of aquatic communities (i.e., bacteria, phytoplankton, zooplankton, benthos, amphibians and fish) for which appropriate toxicity data were located. Toxicity data, including for chloride salts other than sodium chloride, are presented and discussed in Evans and Frick (2000); CTVs for the most sensitive endpoints are included in Table 11. Chloride is persistent (conservative) in the environment and, in fact, can be used as a tracer of water movements. Most freshwater organisms are poikilosmotic regulators, allowing their internal fluids to increase in salinity with the increasing salinity of their environment. Thus, these organisms can accumulate salt when their environment suddenly becomes more saline (e.g., when there is a pulse of road salt in their environment). In addition, the impacts of repeated pulsed exposure to high concentrations of chloride is not known. Similar application factors were therefore used in both the Tier 1 and Tier 2 assessments.

*Conclusions for Tier 1 and Tier 2 assessments*

The Tier 1 assessments indicated that risk quotients were greater than 1 for all taxa considered. Accordingly, a Tier 2 assessment was conducted for all taxa. Tier 2 assessments were conducted by reducing the EEV from 10 000 mg/L chloride to 1000 mg/L chloride. Results are presented in Table 11 (given the assumed differences in exposure scenarios between Tier 1 and Tier 2, all Tier 1 quotients are 10 times greater than the Tier 2 quotients). Even if the Tier 2 exposure value was reduced to 500 mg/L chloride based on less conservative exposure estimates, and if geometric mean of the minimum and maximum recommended application factors were used (Evans and Frick, 2000), all quotients would still exceed 1. Tier 3 assessments were therefore done for all groups of organisms considered in Tiers 1 and 2.

3.3.1.2 Tier 3 assessments

Tier 3 assessments include considerations of the distributions of exposures and/or effects in the environment (Environment Canada, 1997). In order to proceed with this approach, all available data on the toxicity of chloride salts were examined (Evans and Frick, 2000). Effects depend on exposure period. Accordingly, the data are divided into four time periods: less than one day, one day, four days and one week. In addition, chronic toxicity (long-term) values were estimated as described later in this section. For each exposure period and corresponding toxicity thresholds, areas where exposure of concern are likely are noted.

*Less than one-day exposure*

Rapid snow melt following application of road salts can deliver pulses of concentrated chloride solutions to aquatic ecosystems. Highly elevated concentrations may last less than a day, with concentrations declining through the melt event. Therefore, it is instructive to examine toxicity data to assess levels at which exposures of less than one day may have lethal effects.

Few studies have investigated the toxicity resulting from short-term exposures to sodium chloride (i.e., exposures ranging from 15 minutes to 12 hours). $LC_{50}$ values ranged from 8767 to 50 000 mg/L sodium chloride or 5318 to 30 330 mg/L chloride (Table 12), with a geometric mean of 10 781 mg/L chloride. Salt concentrations at the upper end of this range have been associated with direct road runoff in urban areas and other heavy traffic areas (Evans and Frick, 2000). Concentrations at the lower end of the range have been associated with storm sewers and small urban streams during periods of high road salt application rate (Bubeck *et al.*, 1971; Hawkins and Judd, 1972; Cherkauer, 1976) and with ditches (Champagne 1978). Concentrations of this magnitude also have been noted in wetland areas, which have been adversely impacted by leakage from road salt depots (Ohno, 1990), and in groundwater and leachates from road salt storage depots (Morin, 2000).

The evidence suggests that direct runoff of road salt can lead to effects to a wide variety of organisms over relatively short exposure times. The environments in which this is most likely to occur are those in close proximity to highways or storage depots where relatively little dilution of the road salt has occurred.

*One-day exposure*

Road salts may persist in the environment in a relatively concentrated form for some period of time. For example, during melting events, chloride concentrations may increase in ditches and streams and remain elevated for a day or more. Chloride may also be flushed from stream banks during spring, summer and autumn storms. Accumulated chloride at the bottom of urban lakes may be flushed from the lake during spring and summer overturn. All of these events may result in brief (e.g., 1-day) exposures to elevated chloride concentrations.

Six laboratory studies were located which determined 24-hour $LC_{50}$s (Figure 20; Table 13). Concentrations ranged from 2724 mg/L sodium chloride (1652 mg/L chloride) for the cladoceran, *Ceriodaphnia dubia*, to 14 100 mg/L sodium chloride (8553 mg/L chloride) for bluegill sunfish, with a geometric mean of 3746 mg/L chloride. Chloride concentrations at the upper end of this range have been observed for road runoff in heavily salted areas. Concentrations at the lower end of the range, 2000 mg/L chloride, have been observed for urban streams in heavily salted areas such as the metropolitan Toronto area. Thus, it is possible that brief pulses of road salt could have adverse impacts in urban areas in Canada where road salt is heavily applied and where organisms are not able to escape such pulses. Creeks and roadside ditches are the most vulnerable to such impacts. Chloride concentrations in the 1600 to 8500 mg/L range have been observed in impacted areas near salt depots where there has been significant leakage from the salt piles. Because such contaminated waters may move slowly, exposure times are likely to be longer than one day. Chloride concentrations in the 1600 to 8500 mg/L range also have been observed in snow removed from salted roads. If large amounts of this snow were dumped into a relatively small and slowly flowing water body (e.g., a stream or marsh), some organisms may experience toxic impacts.

It is not known how often and where this one-day toxicity occurs in the environment. However, it would appear to occur most frequently in heavily urbanized areas of greatest use of road salts. These events may also occur near road salt storage depots and yards and from melting snow dumps.

*Four-day exposure*

Acute or short-term toxicity studies typically are conducted over periods of up to 96 hours (4 days) and measure mortality (Lee *et al.*, 1995). For short-lived organisms such as algae, a reduction in cell growth relative to the control population may be measured over such a test period, and these four-day studies can be considered chronic studies. However, at the community level, longer exposure times would be required to measure changes in algal species

succession and composition. Four-day exposure scenarios are most applicable to stream and river situations where aquatic organisms are exposed to relatively brief pulses of elevated chloride concentration. Accordingly, lethality data for relatively long-lived organisms (zooplankton, benthos, fish and amphibians) were examined to determine the concentrations at which chloride was toxic. The four-day toxicity data set was increased by including three-day toxicity data, using conversion factors based on Cowgill and Milazzo (1990) (Evans and Frick, 2000).

For a four-day exposure, $LC_{50}$s ranged from 1400 mg/L chloride for the cladoceran *Daphnia pulex* to 13 085 mg/L chloride for the black eel stage of the American eel, with a median of 4026 mg/L and a geometric mean of 4031 mg/L chloride (Table 14, Figure 20). There was a large overlap in the one-day and four-day toxicity curves, primarily due to the low number of available 24-hour studies.

Concentrations of 1400 to 3000 mg/L chloride typically have been associated only with urban creeks and rivers in relatively densely populated areas such as the Toronto area. Moreover, concentrations in this range in creeks and rivers may occur infrequently, even during winter (Evans and Frick, 2000). Nonetheless, as previously noted, chloride concentrations in the 1000 to 3000 mg/L range have been associated with ditches and with wetlands contaminated by road salt storage depots. It is probable that organisms inhabiting such saline stationary waters can experience significant stress in a matter of days.

Schroeder and Solomon (1998) conducted a formal investigation of chloride concentrations and toxicity at three stations on the Don River. Chloride concentrations from November 1995 to April 1996 ranged up to about 950 mg/L at site 1, up to about 2600 mg/L at site 2, and up to about 1150 mg/L at site 3. Based on acute lethal toxicity data ($LC_{50}$) for 13 fish and 7 invertebrate taxa ranging from about 1000 to 30 000 mg/L, the investigators estimated that 90% of the fish species would be expected to be protected from acute effects of chloride toxicity at least 90% of the time at two of the sites and at least 85% of the time at the third site. This means that two species, with $LC_{50}$s of about 1000 mg/L and ca. 2700 mg/L, would experience lethality related to chloride stress some 10–15% of the time at these three sites in the Don River.

Maximum chloride concentrations in creeks in the Toronto Remedial Action Plan Watershed have been measured at concentrations as high as 1400 mg/L to 4310 mg/L (Evans and Frick, 2000), greater than the values reported in Schroeder and Solomon (1999). Thus, based on Schroeder and Solomon's study, it is possible that aquatic organisms inhabiting these waters are acutely stressed by roadsalt-containing highway runoff at least 10% of the time during the winter period. This 10% value is likely to be an underestimate for a number of reasons. First, because sampling frequency in these rivers has not been intense, it is probable that even higher chloride levels do occur on occasion. Second, laboratory studies are available for a limited number of organisms which may not reflect the full range of sensitivities to chloride stress. In addition, laboratory studies are conducted on healthy, well-fed animals, while biota

exposed in the environment experience significant periods of low food availability, thermal stress and other stresses, particularly during winter. Finally, road salt runoff can contain a variety of other contaminants that also may contribute to toxic stress.

*Seven-day exposures*

A few seven-day studies are available which considered mortality as well as growth and fecundity (Table 15). These data provide some insight to toxicity in waters with slow exchanges (e.g., ditches, wetlands, ponds and small lakes).

These experimental data reveal that, as exposure time increases, non-lethal effects such as reduced growth and reproduction begin to be observed as animals and diatoms are stressed by higher salinities. The seven-day $EC_{50}$ data are plotted on Figure 20, using the lowest value for a given species and life history stage from Table 15. These data show that $EC_{50}$ concentrations range from 874 to 3330 mg/L chloride for seven-day exposures with a geometric mean of 1718 mg/L, compared to 2288 mg/L for the seven-day $LC_{50}$ data. Concentrations of this magnitude have been associated with ditches, urban creeks, urban rivers and in small urban lakes in areas such as Toronto. For example, the median December to February chloride concentration in Mimico Creek was ca. 840 mg/L over the 1989 to 1995 period; creeks such as Etobicoke and Highland have elevated chloride concentrations in this range during some winter periods (Evans and Frick, 2000). Small urban lakes that have chloride concentrations in this range may develop anoxic bottom waters, another source of stress to the aquatic community. Chloride concentrations in this range may occur in wetlands near road salt storage depots and may also be expected to result in toxic stress to aquatic communities.

*Chronic toxicity*

Most toxicity studies were conducted over periods of one week or less, providing estimates of the vulnerability of the aquatic ecosystem to brief pulses of chloride concentrations (i.e., organisms living in streams, rivers and ditches). However, organisms living in more stationary (lentic) waters, such as wetlands, lakes and ponds, may experience elevated chloride concentrations for considerably longer periods of time. During this period, non-lethal effects may manifest themselves in reduced growth and reproductive rates, increased metabolic rates, etc. Unfortunately, few laboratory studies have investigated long-term effects.

Two studies were located which investigated chronic toxicity (Birge *et al.*, 1985; Spehar, 1987). These studies allow for the calculation of an acute:chronic toxicity ratio which can then be applied to the four-day $LC_{50}$ data. Birge *et al.* (1985) determined the NOEC and LOEC toxicity of chloride to fathead minnow (32-day test) and *Daphnia pulex* (21 days). For *D. magna*, the NOEC for reproduction was 314 mg/L while the LOEC (27% reduction in reproduction or number of offspring) was 441 mg/L. The geometric mean of these two values is 372 mg/L. The 48-hour $LC_{50}$ for *D. pulex* was 1470 mg/L, giving an acute:chronic ratio of

3.95. If the 48-hour $LC_{50}$ is adjusted to a 1143 mg/L 96-hour $LC_{50}$ using a 1.28 correction factor (from Cowgill and Milazzo, 1990), this value can be lowered to 3.07.

Birge *et al.* (1985) reported that the NOEC for the 33-day early stage test for fathead minnow was 252 mg/L chloride and the LOEC (9% reduction in survivorship) was 352 mg/L, giving a geometric mean of 298 mg/L chloride as estimated chronic value. The four-day acute toxicity was 6570 mg/L giving an acute:chronic ratio of 22.1. The U.S. EPA (1988) included the results of the Birge *et al.* (1985) study in assessing chronic toxicity but used 353 mg/L (9% reduced survival) and 533 mg/L (15% reduction in survival) to calculate the chronic concentration (433 mg/L) and acute:chronic ratio (15.2).

U.S. EPA (1988) cited a study by Spehar (1987) for early life stages of rainbow trout. All trout were killed at a concentration of 2740 mg/L while survival was 54% at 1324 mg/L and 97% or higher at 643 mg/L or less. No further details are provided on this chronic study. U.S. EPA estimated the chronic value at 922.7 mg/L (the geometric mean of 1324 and 643) and the acute:chronic ratio as 7.31.

The U.S. EPA, which uses the Spehar *et al.* (1987) study and a lower value for Birge *et al.*'s fathead minnow study, estimated a geometric mean acute:chronic ratio of 7.6. If an estimated four-day $LC_{50}$ is used for *D. pulex,* as described above, this mean becomes 6.98. Birge *et al.* (1985) and U.S. EPA (1988) calculated the geometric mean of the various chronic ratios to estimate a Final Chronic Value for exposure to chloride. Birge *et al.*'s study provides a concentration estimate of 333 mg/L while the U.S. EPA study provides an estimate of 226.5 mg/L. U.S. EPA also estimated a Final Acute Value by calculating the geometric means of acute toxicity data first at the species and then at the genus level. The most sensitive genus was *Daphnia* providing a Final Acute Value of 1720 mg/L.

A mean acute:chronic ratio of 6.98 is used to predict the chronic values for the organisms shown in Figure 20, based on data for the four-day exposure studies. This curve represents the range of values at which lethal effects may be expected for organisms with long-term exposure to elevated chloride concentrations. Concentrations range from 210 to 1900 mg/L chloride, with a geometric mean value of 578 mg/L. Chloride concentrations in this range have been observed frequently for salt-impacted creeks, rivers and lakes in urban areas and in lakes and wetlands contaminated by leakage from road salt depots.

*Short- to long-term toxicity*

A family of curves can be prepared based on chloride toxicity data following four-day, seven-day and predicted long-term (chronic) exposures (Figure 21). One-day and less than one-day data are excluded because studies were few in number. Data are plotted on a linear-log scale with 95% confidence intervals around each curve. A log-logistic model was used in the curve fitting (Environment Canada, 1997b).

Based on the predicted data, it can be expected that 5% of species would be affected (median lethal concentration) at chloride concentrations of about 210 mg/L (Table 16), while 10% of species would be affected at chloride concentrations of about 240 mg/L.

As previously noted, organisms in the environment may be more susceptible than indicated by laboratory studies, given the hardiness of test species, health of test organisms, other environmental stressors, etc. Therefore, this family of curves may underestimate stress resulting from elevated chloride concentrations from road salt in the natural environment.

### *3.3.2 Field evidence of population or ecosystem effects*

Faunistic studies conducted in fresh and salt waters have shown a gradual loss in the number of fresh water taxa as salinity increases (Figure 22) (Wetzel, 1983). In general for freshwater species, the number of species decreases as salinity increases, with the greatest and most rapid decrease in species numbers at chloride ion concentrations of 1000 to 3000 mg/L. Accordingly, saline lakes generally contain a lower number of species compared to fresh water lakes, with fish typically being absent from meso- and hypersaline lakes due to osmotic stress (Goldman and Horne, 1983; Wetzel, 1983).

This section discusses field evidence of effects of road salts on the biological components of streams and rivers, wetlands and lakes in Canada. The majority of studies found relating to the effect of road salts were conducted in Ontario and Quebec and were based on investigations of the use of road salts in winter for the de-icing of roads. Since relatively few studies were available, studies conducted in the United States were also considered. Extensive discussion of these and other studies is presented in Evans and Frick (2000).

#### 3.3.2.1 Streams and rivers

Several studies investigated the impacts of road salts on stream ecosystems. Dickman and Gochnauer (1978) studied the effects of exposure to sodium chloride on the density of bacteria and algae in Heyworth Stream, near Heyworth, Quebec, between July 24 and October 1, 1973. Sodium chloride was added at four locations along the stream to maintain chloride concentrations of 1000 mg/L (1653 mg/L NaCl). Sodium chloride concentrations at the control site were 2 to 3 mg/L. The stream was described as shallow and fast flowing and densely shaded. Artificial substrates (tiles) were placed in the creek at the experimental site and at an upstream control and recovered at weekly intervals. The treated site had lower algal diversity and lower standing crops of photosynthetic periphyton or algae, which was related to osmotic stress. Auxospore (a resting stage) formation of the diatom *Cocconeis placentula* were noted at the treated site on day 28 but not at the control site; auxospore formation is often triggered by environmental stress. Density of bacteria was greater at the treated site, which was attributed to a reduction in the grazing pressure on the bacterial population because of the reduced number of grazers, such as flagellates, ciliates and rhizopods. The incidence of diatom parasitism was lower

at the treated site than at the control site, possibly because the sodium chloride inhibited fungal growth, as indicated by other researchers (Kszos *et al.*, 1990; Rantamaki *et al.*, 1992).

Overall, these studies suggest that continuous exposure to chloride concentrations as low as 1000 mg/L (1653 mg/L NaCl) for time periods as short as one week can result in changes in stream periphyton communities. Furthermore, the periphyton community may not recover from these stresses, with community composition continuing to remain different from upstream controls one month after continued exposure to this stress. This further suggests that pulses of sodium chloride–laden water during spring melt will have pronounced effects on the periphyton community as will the continued release of high concentrations of sodium chloride from stream banks during summer and autumn months. Periphyton form the base of the food web in many creeks, being grazed upon by invertebrates, which in turn serve as forage for fish. Reduced periphyton algal concentrations may have adverse effects at higher trophic levels. Leaf litter is another important source of food for stream communities. However, invertebrates obtain their nutrition from the microbial and fungal community rather than the litter itself. Reduced fungal biomass resulting from increased sodium chloride concentrations may also impact invertebrate, forage fish and, ultimately, predatory fish communities.

Demers (1992) investigated the effects of elevated chloride levels on the aquatic macroinvertebrates inhabiting four streams near the town of Newcomb in the Adirondack region of northern New York. All four streams were located along a 2-km stretch of state highway 28N. Chloride concentrations in the creeks were measured weekly, yielding an overall mean concentration of chloride in upstream locations of 0.61 mg/L compared to 5.23 mg/L in downstream areas. Artificial substrates were placed in riffle or fast-flowing sections of the stream upstream and downstream of the highway. Samplers were within 50 to 100 m of the road and were left in place between April 22 and June 3, 1988, at which time they were recovered to characterize the colonizing invertebrates. Benthic diversity was lower in downstream than upstream sites. There was an increase of Chironomidae in downstream sites, while Perlodidae (a stonefly family) and Ephemerellidae (a mayfly family) declined downstream of the highway. A similar increase in chironomid and decrease in mayfly and stonefly dominance was observed in the Humber River between November, when road salt had not yet been applied, and the following March, after road salt had been applied, near an Ontario road (Kersey, 1981).

Williams *et al.* (1997) detected significant variations in macroinvertebrate community structure related to different concentrations of chloride in 20 groundwater-fed springs in southeastern Ontario. The chloride content of these springs ranged from 8.1 to 1149 mg/L. Tipulidae and Ceratopogonidae were two taxa associated with springs containing higher chloride concentrations, whereas taxa such as *Gammarus pseudolimnaeus* (an amphipod) and Tubellaria (a flatworm) were found only in springs with low chloride concentrations. The higher chloride concentrations in some of the springs originated from groundwater that apparently had been contaminated by road salt.

Blinn *et al.* (1981) investigated the seasonal dynamics of phytoplankton at three locations along the Chevelon Creek system in Arizona. The chloride concentration at site 1 was 88 mg/L at baseflow compared to 900 to 1100 mg/L at site 3, located 10.8 km downstream of site 1 and 3.5 km downstream of site 2 (chloride concentration at site 2 was not given). The elevated chloride concentration at site 3 was due to numerous seeps and springs from the canyon wall. There were marked differences in phytoplankton between the three sites with species associated with differences in salinities.

Leland and Fend (1998) investigated benthic distributions in the San Joaquin River Valley, California. Total dissolved solids concentrations ranged from 55 to 1700 mg/L. Distinct assemblages were observed at the high and low salinities. Ephemeroptera rarely occurred at salinities above 1000 mg/L (600 mg/L Cl).

3.3.2.2 Wetlands

No studies were found on the effect of road salts on Canadian wetlands, while one study investigated the effects of sodium chloride contamination by a road salt storage pile at Pinbook Bog in Indiana (Wilcox, 1982). In 1963, an uncovered sodium chloride storage depot was established overlooking the bog. Salt-laden runoff from the storage pile resulted in major alterations in the bog vegetation within a 2-ha area, as did runoff from the highway. The salt pile was covered in 1972 and, after winter 1980–81, road salt ceased to be stored at this site. Impacts were studied from 1979 to 1983.

Sodium concentrations as high as 468 mg/L and chloride concentrations as high as 1215 mg/L were recorded in interstitial waters of the bog mat in areas of the strongest road salt impact (Wilcox,1982, 1985). These readings were made in 1979, such that higher concentrations may have occurred in earlier years. Chloride concentrations at control sites in 1980 and 1981 were 5 to 6 mg/L. The maximum single daily readings for salt-impacted locations were 1468 mg/L Cl in 1979, 982 mg/L Cl in 1980, 570 mg/L Cl in 1981, and 610 mg/L in 1983, indicating that decommissioning of the storage facility resulted in reductions in loadings and resulting concentrations in the bog, but that the chloride was subsequently largely retained in the wetland.

Native species, such as *Sphagnum* spp. and *Larix laricina*, were absent from the impacted areas of the bog while salt-tolerant species, such as *Typha angustifolia*, invaded the bog. Salinity tolerances of various plant species were defined (Wilcox, 1985) and taxa were shown to be sensitive to NaCl concentrations in bog water as low as 280 mg/L (170 mg/L chloride) (Table 17). As salt concentrations decreased some 50% over 1980 to 83, many endemic bog plants, including *Sphagnum*, recolonized the bog (Wilcox, 1985). *Sphagnum* began growing on low hummocks in areas where interstitial chloride concentrations had dropped to approximately 300 mg/L.

3.3.2.3 Lakes

Few studies are available documenting field impacts of road salts on the biological communities of lakes.

Tuchman *et al.* (1984) used core samples from lake sediments to investigate the impacts of historic salinization on diatoms of Fonda Lake, Michigan. A salt storage facility has been located adjacent to Fonda Lake since 1953; an asphalt pad was added at the salt storage facility in the early 1970s to reduce loss of salt. A reduction in diversity of algal species began in 1960. Diatom diversity reached a minimum in 1968, when a variety of salt-tolerant (or halophilic) taxa attained their highest relative abundance. In later years, diversity increased slightly and some halophilic taxa decreased in relative abundance, suggesting a decrease in salt loading to the lake. Unfortunately, lake salinity was not determined as part of this study. Zeeb and Smol (1991) extended the study of Fonda Lake to scaled chrysophytes. *Mallamonas caudata*, a chloride-indifferent taxon, dominated at all depths in the core. *Mallamonas elongata*, a widely distributed taxon found more commonly in eutrophic and alkaline waters, and *Mallamonas pseudocoronata*, a chloride-intolerant taxon, declined during the period when chloride concentrations apparently were highest. *Mallamonas tonsurrata*, which occurs mainly in eutrophic lakes, became more abundant during this period. Major shifts in diatom and chrysophyte assemblages were associated with relatively small changes in salinity (i.e., from about 12 to 235 mg/L chloride, or about 20 to 387 mg/L NaCl).

Recent limnological studies have begun to investigate community structure in a wide variety of lakes and as a function of a number of limnological variables, such as conductivity, nutrient concentrations and major ions. Rott *et al.* (1998) investigated periphyton assemblages in the Grand River, Ontario, where chloride concentrations ranged from 7.7 to 85.0 mg/L and conductivity from 180 to 540 µS/cm. Canonical correspondence analysis showed that the largest portion of variability in species composition in the river over the study period could be explained by a seasonal gradient related to temperature and latitudinal gradients of nitrite-nitrate, conductivity and chloride. Phosphorus, ammonia, pH, turbidity and oxygen were of lesser importance.

Dixit *et al.* (1999) assessed changes in water quality in the northeastern United States using diatoms deposited in lake sediments as indicators of change. The composition of diatoms in the surface sediments was related to current water quality parameters including pH, chloride and total phosphorus concentrations. Optima were developed for 235 of the common species (Table 18). Based on analyses of diatoms communities, marked deterioration in water quality was noted in hundreds of lakes. In these lakes, phosphorus and chloride concentrations clearly were higher in modern than in pre-industrial times. Moreover, there has been a marked increase in the number of eutrophic lakes in the Coastal Lowlands/Plateau. This increase in the trophic status of these lakes was associated not only with increasing phosphorus concentrations but also chloride ions. Sodium and chloride concentrations were highly correlated in these lakes, suggesting that increased chloride concentrations were associated with road salting. However, it

was also recognized that agriculture, silviculture and urbanization can affect increases in chloride concentration. Nonetheless, it is already apparent that diatoms have optima chloride concentrations and deviations in these concentrations affect changes in species composition. This also must occur for other organisms such as other algal groups, plants, benthic invertebrates and zooplankton.

The recent research of Dixit *et al.* (1999) is highly suggestive that road salt has a major role in changes in diatom assemblages in the northeastern United States. This, combined with studies, such as Crowther and Hynes (1977), Dickman and Gochnauer (1978), Smol *et al.* (1983), Wilcox (1985) and Zeeb and Smol (1991), suggest that increases in chloride from pre-industrial baseline levels of 10 mg/L or less to concentrations of 200 to 1000 mg/L may have measurable impacts on aquatic ecosystems.

### *3.3.3 Abiotic effects*

Chloride salts can affect aquatic systems through interactions with abiotic components of the environment. Notably, chloride salts tend to be more soluble than carbonate salts and can thus, through various reactions, enhance the mobility of trace metals in aquatic ecosystems. Increased salt loadings can affect water density, thereby affecting mixing processes in lakes and thus disrupting the ecological functioning of that ecosystem.

#### 3.3.3.1 Availability of metals

Increased concentrations of chloride salts in surface water systems can lead to the release of metals from sediments and suspended particulate matter. By competing for particulate-binding sites, sodium chloride acts as an enhancer of dissolved and potentially bioavailable trace metals such as cadmium, copper and zinc (Warren and Zimmerman, 1994). Cadmium, copper and zinc are acutely toxic to aquatic organisms at concentrations as low as 0.001 mg/L cadmium (rainbow trout), 0.0065 mg/L copper (*Daphnia magna*) and 0.09 mg/L zinc (rainbow trout) (CCME, 1991). High concentrations of salts in sediment porewater were shown to augment the concentrations of dissolved heavy metals (e.g., cadmium) and resulting toxicity to a benthic invertebrate *Hyallela azteca* (Mayer *et al.*, 1999). Wang *et al.* (1991) found that 709 mg/L chloride (or 0.02 M) substantially enhanced the release of mercury from freshwater sediments. Mercury can be acutely toxic to invertebrate species and fish in concentrations as low as 0.002 mg/L and 0.02 mg/L, respectively (CCME, 1991) and, when present in its methylated form, accumulates in the tissues of fish. Sodium chloride also enhances mercury mobilization from soils (McLeod *et al.*, 1996).

#### 3.3.3.2 Lake meromixis

Most lakes undergo vertical mixing, resulting in an exchange of deep and surface waters. Such exchanges are important for transferring oxygen-rich surface water to the deeper regions of the

lake. In the absence of such exchanges, deep waters can become anoxic. Vertical exchanges also are important in transferring nutrients regenerated in the deeper regions of the lake to the surface where they become available to the phytoplankton community. Vertical mixing is driven by the winds, which mix surface waters down to depths dependent on lake fetch, surrounding topography and water temperature. Vertical mixing also is driven by changes in water temperature. In regions where winter water temperatures decline to below 4°C (maximum water density), spring warming is accompanied by an increase in water density, promoting the vertical exchange of warmer, nearshore waters with offshore, colder and less dense deep waters. In autumn, lake cooling is accompanied by an increase in water density and similar inshore–offshore and vertical exchanges of waters.

Meromixis occurs in lakes when conditions develop which prevent the vertical exchange of surface and deep waters (Wetzel, 1983). This occurs when a sufficient gradient exists in salinity to override the effects of seasonal variations in water temperature on density and lake mixing. Road salts, by entering lakes through surface flow (overland runoff, ditches, streams) or groundwater discharge (seeps, springs), has the potential to impair the normal circulation of lakes. Small, moderately deep lakes will be the most vulnerable to such meromixis, especially in areas of heavy road salt application. Larger lakes are less vulnerable because the intruding salt-water plumes experience greater dilution as they flow along the lake floor toward the deeper regions of the lake. In addition, larger lakes have greater fetches and hence more powerful wind-driven currents and other water exchanges.

The formation of meromixis can have a number of impacts on lakes. The low oxygen conditions which develop below the chemocline can result in the loss of all but the most resilient of deep-water benthic species. Zooplankton may be excluded from their deep-water daytime refuges, being forced to live in the brighter surface layers where they may be more vulnerable to size-selective fish predation. Hypolimnetic fish such as lake trout may also be adversely affected. The onset of lake meromixis will affect sediment water exchanges. Phosphorus and various metals are more readily released from poorly oxygenated than from well-oxygenated sediments (Wetzel, 1983). This increase in phosphorus release from the sediments may enhance the productivity and eutrophication of the lake, particularly if there is sufficient exchange at the chemocline (Smol *et al.*, 1983). Furthermore, regenerated nitrogen will be dominated by ammonia rather than nitrate.

Few studies have been carried out that documented meromixis association with road salts. The diversity of benthic invertebrates decreased with the anoxic bottom conditions which developed in Lake Wabekayne, a storm-water impoundment in Mississauga, Ontario (Free and Mulamoottil, 1983). Chloride concentrations were elevated from approximately February to April (e.g., 282 mg/L Cl in February 1979), particularly on the bottom of the lake. Concentrations in August 1979 were much lower at 50 mg/L. Smol *et al.* (1983) investigated the impact of cultural disturbances on Little Round Lake, a small meromictic lake on the Canadian Shield in central Ontario. Relatively recent development of meromictic conditions were associated with road runoff and seepage from a salt storage shed. Salt concentrations in

the monimolimnion were 58.4 mg/L sodium and 103.7 mg/L chloride. Road salts were associated with the meromictic conditions described by Kelly *et al.* (1976) in Chocolate Lake, Nova Scotia, with chloride concentrations ranging from 189 to 330 mg/L.

### *3.3.4 Conclusions for surface water ecosystems*

Toxic effects have been associated in the laboratory with exposures to chloride concentrations as low as 400 mg/L for non-lethal effects (fungi) and 874, 989 and 1068 mg/L for median lethal effects (fathead minnow embryos, rainbow trout egg/embryos, daphnids, respectively). The NOEC for the 33-day early stage test for survival of fathead minnow was 252 mg/L chloride, with a LOEC (9% reduction in survivorship) of 352 mg/L. Modelling using acute to chronic ratios indicates possible lethal effects at concentrations as low as 210 mg/L chlorides for daphnids. About 5% of species would be affected (median lethal concentration) at chloride concentrations of about 210 mg/L, while 10% of species would be affected at chloride concentrations of about 240 mg/L. By comparison, Final Chronic Values for chloride were calculated to be 333 mg/L by Birge *et al.* (1985) and 226.5 mg/L by U.S. EPA (1988). While toxicity thresholds are greater for exposures of short duration, concentrations of chlorides associated with road salts have been shown to exceed toxicity thresholds for exposures ranging from less than a day through to long-term exposure.

Changes in populations or community structure can occur at lower concentrations. For example, 13 species of diatoms have been shown to range in their growth optima from 0.5 to 40 mg/L chloride, and shifts in populations in lakes were associated with concentrations of 12 to 235 mg/L.

Evans and Frick (2000) did find evidence that potassium and chloride salts were more toxic than sodium. Also, fish appeared to be less sensitive to calcium chloride and the converse for invertebrates although the data sets were small. Although the focus of the assessment was primarily sodium chloride, potassium chloride and magnesium chloride salts appear to be as toxic or even more toxic than sodium chloride.

It is considered that concentrations of chloride associated with road salts may have immediate or long-term harmful effects on surface water systems, based on frequent exceedences of effect thresholds in the environment and on field evidence of possible ecosystem population effects. In addition, by increasing metal bioavailability, and by affecting density gradients in lakes, road salts may have a major impact on lake ecosystems, notably in terms of depth-dependent availability of oxygen and nutrients, and thereby may constitute a danger to the environment on which life depends.

## 3.4 Soils

### *3.4.1 Evaluating extent of soil salinization resulting from road salt application*

This section summarizes the information presented in the report prepared by Morin *et al.* (2000) on the extent of soil salinization due to road salt application. The report presented soil maps for all provinces in Canada. This mapping effort is complemented with a few case studies designed to show how soil salinity changes dynamically in salt-affected areas, with short distances from point and line salt sources, and with season. The salts that are examined are mainly composed of $Na^+$, $Ca^{2+}$, $SO_4^{2-}$ and $Cl^-$ ions. Contributions due to other ions such as potassium and magnesium are neglected because these generally contribute little to overall soil salinity in most locations.

Mapping of road salt inputs and salt concentrations in soils was done in three ways:

1. as spatial averages compiled for Level 2 watersheds;
2. as spatial averages at the municipality level; and
3. at the road level (mainly principal roads and expressways as well as secondary roads).

This three-way mapping effort was chosen to estimate:

- expected average concentrations in soil solutions based on total road and atmospheric salt inputs per Level 2 watershed;
- expected average concentrations in soil solutions based on total road and atmospheric salt inputs per municipality area; and
- expected average concentrations in soil solutions based on total road and atmospheric salt inputs per soil in immediate road vicinities.

In general, expected average Level 2 soil salt concentrations due to road salt loadings are lower than area-wide municipality averages, and area-wide municipality averages are lower than road soil averages. To quantify these averages, information contained in various national, provincial and municipal databases was compiled to determine:

- local road salt applications, by municipality and county;
- local atmospheric deposition regarding precipitation, air temperature and wet $Na^+$, $Ca^{2+}$, $Cl^-$ and $SO_4^{2-}$ deposition (a dry deposition database does not yet exist; including dry deposition further adds to overall salt loadings, especially in the Atlantic Region on account of sea spray); and
- local soil depth, clay content and organic matter content.

There is a connection between soil salinity and surface water salinity, because most surface waters receive direct input from soils as a result of runoff, interflow, soils percolation

and base flow. Similarly, downslope soils often receive seepage water from higher surface water locations. Gradual dissolution of easily weathered soil and rock minerals further contributes to downslope soil salinization, as do agricultural and horticultural fertilizer applications, and seepage from domestic and industrial sewage. Evaporation of water from dry soils in arid regions such as the Prairie Provinces also contributes to soil salinity, which — in the extreme — leads to above- and below-ground salt accumulations, especially in landscape depressions and on hillslope seeps. This section focusses on the extent to which road salt applications contribute to the overall salinity in soils.

### 3.4.1.1 Definitions and equations

Compiled data on atmospheric $Na^+$, $Ca^{2+}$, $Cl^-$ and $SO_4^{2-}$ loadings refer to volume-weighted ion concentrations (wet deposition only), either in mg/L or meq/L. Salt loadings, in contrast, are generally expressed in terms of g/($m^2$ yr) or kg/(ha yr). In this report, atmospheric and road salt loadings are converted into total dissolved salt (TDS) concentrations in soil solutions by dividing the calculated combined salt loadings with the expected soil percolation rate, where:

| **soil percolation rate (mm/yr)** | = | **precipitation rate (mm/yr)** | - | **actual evapotranspiration rate (mm/yr)** | - | **surface runoff (mm/yr)** |
|---|---|---|---|---|---|---|

For simplicity, soil percolation rates are estimated from:

**soil percolation rate (mm/yr) ~ stream discharge rate (mm/yr)**

where stream discharge rates are obtained from watershed-specific hydrometric discharge observations. For the mapping effort, expected soil percolation rates are therefore set equal to stream discharge rates. Maps located in Morin *et al.* (2000) depict:

- mm of stream water discharge at a national scale, as obtained from Natural Resources Canada; and
- m of stream water discharge per Level 2 watershed (as obtained from the national stream discharge map).

Watersheds with highest runoff coefficients occur along the Pacific and the Atlantic coasts. Watersheds located in the southern part of the Prairie Provinces have the lowest quantity of runoff to dissolve and dilute the salts. Areas with low rates of runoff are important to identify because these areas have high road salt concentrations in runoff.

The soil solution estimates for TDS loadings and related ion concentrations can then be used to calculate:

- Total Cations (TC) and Total Anions (TA) (in meq/L);
- Soil Electrical Conductivity (EC) (in mmho/cm, or mS/cm);
- Osmotic Potential (OP) (in bar);

- Sodium Absorption Ratio (SAR) (dimensionless);
- Exchangeable Sodium Ratio (ESR) (dimensionless);
- Exchangeable Sodium Percentage (ESP) (in %);
- Exchangeable Sodium Content (ESC) (in meq/100 g oven-dry soil);
- Soil Clay and Silt Dispersion (SCD) (as % of soil clay content (SCC)); and
- Relative changes in soil Hydraulic Conductivity (RHC) (dimensionless).

For the mapping of these parameters, it was also essential to obtain national soil information on:

- Soil Clay Content (SCC) (as % of mineral portion of soil (particulate matter < 2 mm));
- Soil Organic Matter (SOM) (in %); and
- Cation Exchange Capacity (CEC) (in meq/100 g oven-dry soil).

3.4.1.2 Mapping calculated salt loadings and related impacts of soil salinization

Estimates for total salt loadings were obtained from provincial agencies by maintenance district. Municipal loadings were treated as point data. These data were then attributed to:

- Municipal areas
- Level 2 watersheds
- Provincial-level roadway right of way

Maps were developed to show, per Level 2 watershed area, per municipality area, and per area of provincial roadway right of way:

- combined atmospheric and road salt loadings;
- related values for electrical conductivity, osmotic potential and total dissolved solids in soil solutions;
- related values for ESR and exchangeable sodium of soil solutions; and
- calculated values for potential soil dispersion and subsequent potential for soil permeability reduction.

Likely salt-induced impacts on soils refer to substantial reductions in soil osmotic potentials, soil swelling, reduced soil stability (loss of soil structure), decreased soil permeability, increased potential for soil erosion, increased clay and silt dispersion, and increased turbidity in surface waters. All of these impacts increase directly with increasing sodium content in the soil. This is because increased sodium ion contents decrease the affinity that soil particles have for each other on account of the strong affinity between sodium ions and water molecules.

Soils that have a relatively high clay content and receive high sodium inputs will likely show the strongest impacts in the long run (i.e., should receive a high salt hazard rating). To map

where there would be areas with a high salt hazard rating, a simple salt hazard index was obtained by setting:

**Salt hazard index = ESR * soil clay content (in %).**

Locations with highest hazard ratings occur in southern Ontario near the GTA and on and near the Island of Montréal (Figure 23). Other areas in southern Ontario and southern Quebec are also have high ratings.

3.4.1.3 Case studies

Three case studies were conducted at Kejimkujik National Park, Nova Scotia, along select streets in Fredericton, New Brunswick, and in a forested area next to Fredericton's municipal salt depot (University of New Brunswick Woodlot). These studies focussed on:

- providing numbers for the general turnover rate of sodium ions in the soils of headwater basins at Kejimkujik National Park (an environment that is essentially free of road salts but is influenced by sea spray);
- assessing the status of soil salinity underneath lawns next to the curb of select roads, during the fall season; and
- examining how the salinity of surface water changes with distance from the salt depot, by season.

The results of these case studies indicated that:

(i) The ability of soils and watersheds in the Kejimkujik National Park to retain incoming sodium and chloride ions is very low (i.e., sodium and chloride ions are readily flushed through the soils and through the basins of the park). Ion concentrations are highest during early to late fall and lowest concentrations occur at the time of snow melt.
(ii) Along the city streets of Fredericton, generally little sodium remains on the ion-exchange sites in soils next to roadside, during fall. The data indicate that ion-exchangeable sodium is particularly low along most frequently travelled roads. Furthermore, exchangeable sodium concentrations are lower next to curbs than 2 to 3 m away from curbs, indicating that repeated and substantial traffic splashing and road runoff during spring, summer and fall flushes sodium out of the road-side soils.
(iii) Compared to the Kejimkujik National Park, background sodium and chloride ion concentrations in soil solutions and in surface waters are somewhat smaller at the University of New Brunswick woodlot (3 ppm vs. 2 ppm, respectively); sodium concentrations in ditch and stream water varies by location. In ditches, depressed locations have 30 to 40 ppm sodium; well-drained sites have 7 to 8 ppm sodium. In addition, sodium concentrations are highest at and near the salt depot, ranging from 3000 to more than 10 000 ppm. Immediately downslope from the depot is a water reservoir containing sodium concentrations at 100 to 300 ppm. Discharge from this

reservoir gets further diluted with increasing downstream distance. In all of this, season also affects the salt concentrations, as follows:

- salt concentrations are lowest during wet, rainy seasons such as fall and spring at the time of snowmelt; and
- during summer, salt concentrations increase during periods of drought. Highest concentrations occur in June, July and August when increases in salt concentrations spread out away from the depot into the adjacent pond, ditches and streams.

3.4.1.4 Discussion

Road salt application effects on soil physical and chemical parameters such as osmotic potential, electrical conductivity, soil permeability, soil dispersion and exchangeable sodium ratio (see Morin *et al.*, 2000 for detailed information on other physical and chemical parameters) are all calculated to be highest in areas next to salt depots and roads receiving salt inputs. At the municipal level, soil impacts can be expected to vary greatly depending on the density of road network, on local conditions, and on actual locations of road salt application. For example, in all highly paved urban areas, road salt applications are expected to produce salt concentrations in soils and surface waters at levels similar to those calculated for the Island of Montréal. Figure 24 shows TDS, OP and EC of average soil solution and surface water on (1) an averaged watershed basis and (2) a municipal level. Results of this comparison indicate that when total road salt loadings are averaged over a watershed, the average concentrations in runoff and soil solution are generally lower than when they are associated only with the boundaries of urban municipalities. The same parameters were calculated for a roadway right of way (Figure 25) using data on provincial salt loadings by maintenance district. Overall, Figure 25 indicates that areas immediately surrounding the right of way can be subject to very high impacts. While the seasonally sustained degree of soil salinization due to road salt applications would be low for rural areas and suburbs with substantial lawns and open, non-paved spaces, each related soil and surface water salinity parameter would be above natural background levels.

The process of salt dilution through subsequent precipitation and traffic splashing is quite important in terms of allowing much of the Canadian soil roadscape to recover partially or completely from seasonal road salt applications. Apparently, splashing from roadsides accelerates the leaching loss of winter-accumulated salt. However, during times of high Exchangeable Sodium Percentage (ESP) values and low EC splash water, this effect may have deleterious effects on, for example, soil clay and silt dispersion, which can lead to reduced soil infiltration rates, and hence enhanced soil erosion. This effect would be highest where roadsides are not covered by vegetation. The map in Figure 26 suggests that certain areas in Ontario and Quebec may have roads with elevated ESP values. These values are primarily associated with areas that have high road salt loadings. Figure 26 also suggests that certain areas in the Prairie Provinces may also have high ESP values. While roads in the Prairie Provinces have lower road

salt loadings than in Ontario and Quebec, there is less precipitation to dissolve and dilute the salts.

Underneath paved surfaces, soils may not benefit from seasonal dilution. Salt in these locations likely remains concentrated or accumulates even more because these locations are, at least in part, outside the paths of percolating soil water. These locations, therefore, become a sink and a source of soil salinity: a sink during times of road salt application, and a source later.

Salt concentrations in soil solutions may not necessarily be highest at the time of application, but highest concentrations in soil solutions and surface water may occur later in summer during periods of drought when water evaporates, and when salty water from subsoils seeps back into downslope surface soils and surface water. During times of high precipitation, low EC water will help to flush out briny water from these areas. Along roadsides, frequent splashing during rain events may further accelerate the displacement of briny water and the return to low soil ESP values, but this can occur rapidly only in soils of high permeability.

The overall salt impacts on soils needs to be evaluated in terms of landscape-level source/sink positioning (i.e., distance from road, location of roadside in relation to road — above road, below road, same level as road, upwind from road, downwind from road) and terrain conditions along roads (e.g., open vs. forested). Typically, salts are spread from road to roadside by vehicle spray, dust and runoff. In all of this, soil salinity is expected to increase from ridge tops (recharge areas) to depressions (discharge areas).

Increased soil salinization through road salt applications may affect soil biota (macro and micro flora and fauna). For a simplified summary of expected plant sensitivities and related species-specific threshold tolerances to falling soil osmotic potentials, refer to Figure 27. Figure 27 associates the sensitivity of crops to soil salinity by demonstrating how crop yield decreases with increasing levels of EC. The red boxes in this Figure show the percentage of provincial roadways that have different levels of estimated soil salinity (based on estimated electrical conductivity of average soil solution). Data in this graph suggests that salinity in soil solution alongside the majority of provincial roads may adversely affect species that are "sensitive" to "moderately sensitive" to soil salinity. Other impacts of road salts effects not covered in this section deal with salt induced release of trace metals (e.g., iron, manganese, phosphorus), and base cations (calcium, magnesium, potassium). All of these may have positive or negative effects on soil flora and fauna (i.e., encouraging the growth of certain species in otherwise nutrient-poor ecosystems, or leading to eutrophication of soil and aquatic habitats, depending on local circumstances). For further details see, for example, Bresler *et al.* (1982), Butler and Addison (2000), Brownlee and Mineau (2000) and Cain *et al.* (2000).

Since expected decreases in soil osmotic potential due to increased soil salinization has been mapped, we can now, in principle, undertake species-specific "hotspot" mapping (i.e., produce maps that show where — on the national scale— which species will likely suffer salt threshold exceedances). However, the maps so produced will not provide location-specific

exceedance information because the areas so identified represent municipality-wide road averages. For local pinpointing of highest salt impacts, one would require additional information (i.e., details about local road-specific salt applications and local topography maps to determine the exact locations and extent of local depressions).

Road salt effects on soils are expected to be highly dependent on the extent of vegetative cover. Soils that are bare likely suffer the worst impacts in terms of surface crusting, surface runoff, and clay and silt dispersal. Soils that are originally covered by vegetation will also suffer impacts once the surface vegetation reacts negatively to high negative osmotic potentials in the soil. Here, gradual loss of surface vegetation will lead to increased mineral soil exposure: this leads to gradually decreasing levels of soil organic matter (therefore, increasing soil dispersion and decreasing soil permeability) and increasing soil erosion.

#### 3.4.1.5 Conclusions

Application of road salts can result in deleterious effects on physical and chemical parameters of soils. Highest effects are calculated in areas directly impacted by salt depots and along roadsides. Electrolyte-related impacts affect soil structural stability, soil dispersion, soil permeability, soil swelling and crusting, soil EC and soil OP. Surface waters that come into contact with the salt-affected soils are also affected by receiving briny water enriched with salt-dispersed sediments. All of this has, in turn, abiotic and biotic impacts on the environment. Abiotic impacts primarily deal with loss of soil stability during drying and wetting cycles, and during periods of high surface runoff; biological impacts primarily deal with osmotic stressors on soil macro and microflora and fauna, and salt-induced mobilization of macro and micro nutrients which in turn affect flora and fauna *in situ* as well as seepage areas downslope.

### *3.4.2 Biological effects of road salts on soils*

A comprehensive review of the effects of salt on soil microflora and fauna was compiled by Butler and Addison (2000). There appears to be very little data dealing with road salt exposure and soil microbial communities and/or their activities. Thus, available literature on the metabolic adaptations required for microbial salt tolerance, and on the effects of high soil salinity on agriculturally-important processes, was reviewed and addressed for this assessment, although the originators of the quoted data had very different purposes than those of this document. An additional difficulty is the varied ways of reporting salt exposures in the literature. Soil-to-soil comparisons are typically based on electrical conductivity, water potential or osmotic potential, not added salt concentration, because the ionic composition of different soil solutions varies. However, salt concentrations (mass/liquid vol) are more usually reported in the microbiology literature. Studies involving soil fauna typically report salt inputs as amount/unit area.

### 3.4.2.1 Ecological role of soil biotic communities

The biological communities of soils and sediments are responsible for the degradation and mineralization of organic matter, and cycling of elements (e.g., carbon, nitrogen, phosphorus, sulphur) in these environments. In terrestrial systems, there is only a minor direct contribution to primary production by photo- and chemolithotrophic microbes. However, experiments have indicated that the primary productivity of higher plants is greatly enhanced by the activities of the below-ground microbial and faunal biota (Faber and Verhoef, 1991, Setälä and Huhta, 1991, Setälä *et al.*, 1998). Mycorrhizae are features of nearly all terrestrial plants, with the fungal partner of this symbiotic plant-fungus relationship contributing to nutrient (especially phosphorus) uptake and translocation, and potential protection against plant pathogens, nematodes and toxicants such as heavy metals in the rooting zone (Paul and Clark, 1996). The enzymatic capabilities of the soil microfauna (e.g., protozoa, nematodes) and mesofauna (e.g., mites, wingless insects) are more restricted than those of the prokaryotes and microfungi, so that most of the chemical transformations involved in organic matter decomposition and nutrient cycling are mediated by soil microbes. The contributions of the soil fauna to these processes include more indirect effects such as physical breakdown of litter, dispersal of microbial propagules (including mycorrhizae and pathogens), selective grazing on microbial species and, in the case of macrofauna, modification of soil structure. For example, earthworms, where present, can exert a tremendous impact on soil aeration, aggregate structure, water-holding capacity, and bulk density of soils, as well as influence nitrogen mineralization rates (Lee, 1985).

### 3.4.2.2 Effects on the soil biota

Data on effects of salt on soil organisms are presented by Butler and Addison (2000). Soil bacteria can be quite sensitive to salt. Hattori & Hattori (1980) studied the growth of 40 oligotrophic soil bacteria isolated from various Japanese soils. Two of the 40 bacteria were moderately inhibited by 0.15 g/L sodium chloride (corresponding to approximately 60 ppm sodium and 90 ppm chloride). One bacterium was strongly inhibited by 1 g/L sodium chloride (approximately 400 ppm sodium and 600 ppm chloride), while 17 were strongly inhibited by 5 g/L sodium chloride (approximately 2000 pm sodium and 3000 ppm chloride). Eleven of the 40 bacteria were strongly inhibited by 10 g/L sodium chloride while the remaining 9 were moderately inhibited at 10 g/L. McCormick and Wolf (1980) found that soil nitrification was significantly reduced when 0.25 g/kg (approximately 100 ppm sodium and 150 ppm chloride) or more sodium chloride was present. Sodium chloride at ≥10 g/kg completely inhibited nitrification. Rhizobia, $N_2$-fixating soil bacteria that nodulate important legume crops (e.g., soybean, pea, clover) tend to be salt-sensitive. The generation time of rhizobia, *Bradyrhizobia japonicum*, was increased with exposure to 2.6 g/L sodium chloride (corresponding to approximately 1040 ppm sodium and 1560 ppm chloride) (Upchurch and Elkan, 1977). Earthworms can also be quite sensitive to salt. Earthworms of the species *Eisenia fetida*, died within two weeks when exposed to ≥5 g/kg sodium chloride (Kaplan *et al.*, 1980). McCormick and Wolfe (1980) reported a fairly sharp decline in $CO_2$ evolution from a sandy loam treated for 14 weeks with sodium chloride when sodium chloride exceeded 10 g/kg

(corresponding to about 4000 ppm sodium and 6000 ppm chloride). Soil receiving 100 gk/g sodium chloride did not release detectable $CO_2$.

3.4.2.3 Exposure of soil organisms to road salt

Soil concentrations of sodium and chloride are presented in Cain *et al.* (2000). The highest soil chloride concentration reported was 1050 ppm in a sample taken in the highway median, and the highest soil sodium concentration was 890 ppm in a sample taken 10 m from the highway, both from a study along a four-lane highway in Ontario (Hofstra and Smith, 1984). Concentrations of sodium and chloride decreased rapidly with distance from the road. Concentrations of sodium were below 100 ppm at distances greater than about 20 metres at all reported Canadian sites, while concentrations of chloride were below 300 ppm at distances greater than about 30 metres from the road.

Sodium concentrations of up to 13 100 ppm and chloride concentrations up to 14 500 ppm have been reported in soils at patrol yards (section 2.4.4.2).

3.4.2.4 Environmental assessment

Sensitive soil bacteria are moderately inhibited by sodium chloride at concentrations as low as 0.15 g/L sodium chloride (corresponding to approximately 60 ppm sodium and 90 ppm chloride). Soil nitrification can be significantly reduced at a sodium chloride concentration of 0.25 g/kg (approximately 100 ppm sodium and 150 ppm chloride). Soil concentrations of sodium exceeding 60 ppm have been reported within about 30 metres from the edges of roads in Canada. Soil concentrations of chloride exceeding 200 ppm have been reported within about 200 metres from the edges of roads in Canada.

Concentrations high enough to adversely affect microorganisms and other soil organisms have also been reported for soils at patrol yards.

3.4.2.5 Conclusions

Concentrations of sodium and chloride in soil near the edges of roads in Canada and in patrol yards are high enough to have adverse effects on sensitive soil organisms. How serious these effects might be to soil ecosystem function is very difficult to gauge. Soil microorganisms may have considerable ability to adapt to increased salinity or to re-establish from unaffected areas. The dispersal capabilities of soil fauna such as earthworms is low, as most species are adapted to the relatively high humidity of the soil environment. Where affected areas are small enough, for example, strips of soil adjacent to roads, populations of impacted soil organisms may be able to be re-established quite quickly if the unfavorable salt conditions are abated.

### 3.5 Salts and Terrestrial Vegetation

Information presented in this risk assessment section is taken from the unpublished report, "Critical Review of Effects of Sodium Chloride and Other Road Salts on Terrestrial Vegetation in Canada" (Cain *et al.*, 2000).

Elevated levels of sodium and chloride, in the substrate or soil affect plants in various ways:

1) inhibition of water and nutrient absorption by plants due to osmotic imbalances, resulting in reduced shoot and root growth and drought-like symptoms.
2) nutritional imbalances for some species by disrupting uptake of other nutrients.
3) long-term growth inhibition, and, at higher levels, direct toxicity to the plant cells, manifested in leaf burn symptoms and tissue death.
4) deterioration of soil structure.

Plant symptoms following elevated soil levels of sodium and chloride include general plant decline, reduction in leaf size and plant growth, leaf chlorosis, leaf burn and tissue death. Seed germination can be reduced or delayed as well.

Injury of woody plants along roadsides due to salt spray is the result of tissue drought or desiccation and is related to the penetration of phytotoxic ions of sodium and chloride through the stem, bud and leaf tissues (Barrick and Davidson 1980; Chong and Lumis 1990).

Death of stems and leaf and flower buds, usually on first-year shoots, are the predominant symptoms on deciduous woody plants. Flower buds are more sensitive to salt injury than leaf buds. Conifers exhibit premature leaf-drop and browning of needles. Repeated injury, year after year, reduces the vigour and growth of woody plants.

There have been extensive compilations of ratings of sensitivity of woody plants from various observational and experimental studies. A survey of these woody plant ratings (ornamental and forest species) in the literature indicated that from 29.6 to 50.8% of the plants listed in each report were deemed sensitive to salt, in at least one rating (Sucoff 1975, Dirr 1976, Lumis *et al.* 1977, Thuet 1977, Beckerson *et al.* 1980, Dobson 1991).

Lumis *et al.* (1977), making field observations of plants on Ontario roadsides, rated 30% of 73 species as sensitive to road salt; 7% had severe injury symptoms that could result in plant death. A review of sensitivity ratings of plants commonly used in Canadian landscape plantings (Beckerson *et al.*, 1980), found that 40% of 89 species had been rated as sensitive to road salt.

A survey of the salt tolerance ratings of 32 cultivars or varieties of fruit trees, vines or shrubs, representing commercial crop and landscape plants (Appendix 2 in Cain *et al.*, 2000), indicated that 65% were considered sensitive to salt in at least one rating.

There are 15 principal genera of trees (over 25 species) within Canadian forested regions according to Rowe (1972) and eleven of these have been rated as sensitive to road salt (Section 4.5 in Cain *et al.*, 2000). Looking at individual species listed by Rowe, eight of 15 (53%) have been rated as sensitive to road salt in at least one rating.

### *3.5.1 Conservative environmental assessment*

EC25 and CTV threshold values were estimated from the scientific literature for chloride, sodium and sodium chloride in growing media (soil, soil water or water) and for chloride and sodium in plant tissue. LOEL threshold values were identified for chloride and sodium chloride in growing media and NOEL threshold values were identified for sodium chloride in growing media.

#### 3.5.1.1 Effects threshold values

For the conservative assessment, the values used were the lowest concentrations that were identified in the threshold value analysis (Section 3.6 in Cain *et al.*, 2000) for each type of threshold described above.

These threshold values have been tabulated in Tables 19, 20 and 21 and in Section 3.6 in Cain *et al.*, 2000. The plant species represented include wetland species including rushes, sphagnum moss bulrush, cattails, duckweed; herbaceous species including sedges, grasses, beets; coniferous species including pine, and spruce; and deciduous species including maple, peach and plum. The threshold values ranged from 67.5 to 300 ppm sodium, 215 to 1500 ppm chloride, and 280 to 66,600 ppm sodium chloride in growing media (applied soil solution); from <280 to 17,800 ppm sodium and <4100 ppm chloride in herbaceous tissue following soil or water solution exposure; and 200 to 16,100 ppm sodium, 800 to 70,700 ppm chloride and 7,140 ppm sodium chloride in woody tissue following aerial exposure.

#### 3.5.1.2 Estimated exposure values

The EEV used in the conservative assessment were the highest values extracted from the literature dealing with environmental concentrations in Canada of chloride or sodium in growing media (soil or aqueous) in roadside conditions, or the highest values extracted from the all the literature dealing with concentrations of chloride or sodium found in vegetation growing along salted roadsides. The highest soil chloride concentration reported was 1050 ppm in a sample taken in the highway median, and the highest soil sodium concentration was 890 ppm in a sample taken 10 m from the highway, both from a study along a four-lane highway in Ontario

(Hofstra and Smith 1984). No Canadian references reported soil concentrations of sodium chloride. A value of soil sodium chloride was estimated based on the highest concentration of chloride found in the soil in a highway median, 1050 ppm. which was multiplied by a factor of 1.6485, resulting in a value of 1731 ppm sodium chloride. A second value of soil sodium chloride was estimated based on the highest concentration of sodium found in the soil 10 m from the highway, 890 ppm, which was multiplied by a factor of 2.542, resulting in a value of 2262 ppm sodium chloride. The average of these two values, 1997, was used in the conservative estimation.

In order to estimate the aerial exposure of plants to sodium chloride following road de-icing, references were reviewed that reported concentrations of chloride or sodium in plant tissues at given distances from the road or highway, following exposure to road salt aerial dispersion (refer to Section 2.3 in Cain *et al.*, 2000). Three references were reviewed for tissue concentrations of chloride and sodium. These data included plant tissue samples taken from 10 to 200 m from the road or highway. These references reported studies from Ontario on *Prunus* (peach and plum) and unspecified vegetation. The highest tissue chloride concentration was 11 000 ppm, reported in unspecified vegetation growing 60 m from a four-lane highway in Ontario (Hofstra and Smith, 1984). A second reference reported 9000 ppm in peach, *Prunus persica*, growing 20 m from a four-lane highway in southern Ontario (Northover, 1987). The highest tissue sodium concentration was 6900 ppm, reported in twig tissue of *Prunus persica*, peach growing 20 m from a four-lane highway in southern Ontario (Northover 1987).

#### 3.5.1.3 Quotient Estimation

From Section 3.5.1.2, it can be seen that chloride and sodium have been reported in Canadian soils and in plant tissues at concentrations higher than the effects threshold values presented in Section 3.5.1.1 and in Section 3.6 in Cain *et al.* (2000). Therefore, a detailed assessment of the effects of road salts on terrestrial vegetation is warranted.

### *3.5.2 Detailed environmental assessment*

This Risk Characterization reviews concentrations of chloride and sodium in soils or tissue that produce biologically relevant effects on vegetation and relates these to concentrations found in the Canadian environment. The data presented represents primarily Canadian literature and incorporates threshold values that were presented in section 3.5.1.1 above and in section 3.6 in Cain *et al.* (2000). Reference sites are presented that document effects on vegetation that can be traced to application of road salts.

#### 3.5.2.1 Response to sodium in soil

The range of threshold values for root applied sodium chloride evaluated as sodium was 67.5 to 300 ppm (Table 19 above and Section 3.6 in Cain *et al.*, 2000). The most sensitive plants

reported were two-year old ponderosa pine (*Pinus ponderosa*) seedlings, with a threshold value of 67.5 ppm, based on foliar injury following soil application of a sodium chloride solution (Bedunah and Trlica, 1979). Seed germination rates of prairie grass and broad-leaved wildflower species were reduced by about 60 to 70% and root growth was reduced by up to 73% when plants were exposed to 100 to 400 ppm sodium chloride (about 40 to 160 ppm sodium) (Harrington and Meikle 1992). The EC25 threshold values that were estimated from this study for sodium concentration in soil were 202 to 270 ppm.

The concentration of sodium in soil exceeded the estimated threshold range of 67.5 to 300 ppm in a number of soil samples collected in Canada at a distance of about 30 m or less from the roads (Figure 2.17 in Cain *et al.*, 2000).

3.5.2.2 Response to chloride in soil

The range of threshold values for root applied sodium chloride evaluated as chloride was 215 to 1500 ppm (Table 19 above and Section 3.6 in Cain *et al.*, 2000). The most sensitive plants reported were two-year old ponderosa pine (*Pinus ponderosa*) seedlings, with a threshold value of 215 ppm chloride, based on foliar injury following soil application of a sodium chloride solution (Bedunah and Trlica, 1979). The estimated LOEL for reduction in mean length growth of sphagnum moss, *Sphagnum recurvum*, was 300 ppm chloride (Wilcox, 1984).

The concentration of chloride in soil exceeded the estimated lowest thresholds of 215 to 500 ppm in a number of soil samples collected in Canada at a distance of up to 200 m from the roads (Figure 2.16 in Cain *et al.*, 2000). Concentrations of chloride in soils exceeded 500 ppm only at the edge of the roads. A soil concentration of 1200 ppm chloride was found in the soil behind a patrol yard located along a highway in north-western Ontario (Racette and Griffin, 1989).

3.5.2.3 Response to sodium chloride in soil

The range of threshold values for root applied sodium chloride evaluated as sodium chloride was 280 to 66,600 ppm (Table 19 above and section 3.6 in Cain *et al.*, 2000). The most sensitive reported species were the three-fruited sedge, *Carex trisperma*, and the mountain holly, *Nemopanthus mucronata* [*mucronatus*], which had a salt tolerance limit of 280 ppm (Wilcox, 1986a).

No Canadian references reported soil concentrations of sodium chloride, however, values have been estimated using reported concentrations of sodium and chloride. A value of soil sodium chloride of 1978 ppm was estimated by multiplying the highest concentration of chloride found in the soil in a highway median, 1200 ppm, by a factor of 1.6485. A second value of soil sodium chloride of 2,262 ppm sodium chloride, was estimated by multiplying the highest concentration of sodium found in the soil 10 m from the highway, 890 ppm by a factor

of 2.542. The average of these two values, 2120, was about 10 times the lowest threshold value of 280 ppm.

3.5.2.4 Detailed environmental assessment conclusions

Elevated soil levels of sodium and chloride have been recorded up to 30 m from four-lane highways (Hofstra and Smith, 1984, Davis *et al.*,1992), and up to 15 m from two-lane highways (Davis *et al.*, 1992, Soilcon Laboratories Ltd. 1995). The threshold range of 67.5 to 300 ppm sodium and 215 to 450 ppm chloride in soil would be exceeded in a zone of about 30 m from highways (Figures 2.8 and 2.7 in Cain *et al.*, 2000), depending on the class of road, application rates, local topography and climate. Threshold values have also been exceeded on sites where salty run-off has collected (Racette and Griffin, 1989).

Similarly, elevated tissue concentrations of sodium and chloride have been reported for vegetation growing adjacent to highways in southern Ontario. Tissue concentrations exceeding the lowest threshold values of 575 ppm sodium and 800 ppm chloride estimated for sensitive plant species (Table 21 and in Section 3.6 of Cain *et al.*, 2000) have been reported at distances up to about 120 m from highways for sodium and up to 200 m for chloride.

*3.5.3 Field studies*

A number of Canadian studies have evaluated environmental concentrations of sodium and chloride and plant impacts as a result of de-icing salt application to roads or run-off as a result of handling activities in highway maintenance patrol yards. Some American studies that are relevant to Canada have also been included in this section.

Details about these studies can be found in Section 4.4 in Cain *et al.* (2000).

3.5.3.1 Spread of Halophytic Plant Species

The spread of halophytic species, characteristic of sea coasts and salt marshes, has been recorded along roadsides in Ontario. Catling and McKay (1980) reported the occurrence of 20 salt-tolerant plant species along roadsides in Ontario, of which 4 plant species were reported for the first time in the province. The range of 4 additional species was extended significantly. These species were spreading naturally along highways in response to the use of de-icing salts and the decline of non-adapted vegetation. The sites studied had sodium concentrations in the range of 1000 ppm and growing conditions that that ranged from aquatic, moist, periodically moist to dry. Species that were tolerant of soil sodium levels of 500 to 1000 ppm and were often associated with halophytic species included narrow-leaved cattail (*Typha angustifolia*), common reed-grass (*Phragmites australis*), and weedy species such as annual and perennial sow-thistle (*Sonchus oleraceus*, *Sonchus arvensis*, *Sonchus uliginosus*), common ragweed (*Ambrosia artemisiifolia*), wild carrot (*Daucus carota*) and kochia (*Kochia scoparia*).

Reznicek *et al.* (1976) reported the increase in distribution of *Carex praegracilis*, an alkali-tolerant western species, since it's first observation in Ontario in 1973. The plant was observed in 28 highway locations in 14 counties.

Similar observations of the spread of salt-tolerant species have been made in Michigan, which has a similar climate and flora to southern Ontario (Reznicek, 1980).

3.5.3.2 Grimsby, Ontario,four-lane highway

The effect of distance on salt spray was studied in a number of peach and plum plantings along the QEW, a four-lane, controlled access highway in the Grimsby and Beamsville area of Ontario (McLaughlin and Pearson, 1981). Peach and plum trees were evaluated for terminal twig dieback in April 1980 and 1981.

The chloride and sodium content of the twigs was highest closest to the highway and generally decreased with increasing distance from the highway (Figures 4.15 and 4.16 in Cain *et al.*, 2000). Twig tissue sodium concentration was 2,030 ppm at 45 m from the highway. sodium content was 2,300 ppm at 40 m from the highway.

Twig dieback was greatest in the plants closest to the highway and decreased with increasing distance from the highway (Figure 4.17 in Cain *et al.*, 2000); however, the degree of dieback differed between years and species. Injury was greater on the south side of the highway in April of 1981; peach twig dieback was 288 mm at 22 m from the highway, decreasing to 97 mm at 82 m from the highway. In April 1980, peach twig dieback on the south side of the highway, fell from 91 mm at 36 m from the highway to 8 mm at 82 m from the highway. Twig dieback was correlated with tissue concentrations of sodium and chloride. Twig dieback increased with increasing concentrations of sodium and chloride in the combined peach and plum data (Threshold evaluation, Appendix 8 in Cain *et al.*, 2000).

3.5.3.3 Community changes in a road-salt impacted bog

The effects of sodium and chloride contamination was studied in a Pinhook bog, located in northwestern Indiana, southeast of Michigan City, that had been impacted by road salt runoff (Wilcox 1982, Wilcox 1986a, b). This study is relevant to the regulation of road-salts in Canada since it provides evidence of plant community impacts by elevated salt levels and. Many of the predominant plant species in this bog are native, wetland species that are found in Canada. This part of Indiana is part of the Great Lakes Basin and has the same climatic zone as parts of southern Ontario, the Maritimes and British Columbia.

An uncovered road-salt storage pile had been located on an embankment adjacent to the bog from 1963 to 1972. A protective dome was placed over the salt pile in 1972 to limit runoff. The bog also received runoff from a 1-km stretch of a four-lane highway (Interstate 80/90).

The most severely impacted area had mean salt concentrations as high as 486 ppm sodium and 1215 ppm chloride in the interstitial waters of the peat mat. The pattern of elevated sodium and chloride concentration in the bog was correlated with zones of affected vegetation. The salt concentrations in the root zone decreased each year from 1979 to 1981.

Vegetation evaluations were carried out on the unimpacted and impacted portions of the bog from 1980 to 1983. The salt contamination had resulted in a shift in vegetation species in the impacted areas. Nearly all of the endemic plant species were absent from the portion of the bog with elevated salt levels. They had been replaced with non-bog species dominated by narrow-leaved cattail (*Typha angustifolia*).

As salt levels declined by 50% over the four-year study period, many endemic species returned to the impacted bog. Some of the species that had invaded during the high salt conditions declined, while others such as *Typha angustifolia* and *Pyrus floribunda* remained dominant in parts of the impacted bog.

3.5.3.4 Salt spray from a four-lane highway to peach and plum orchards in southern Ontario

The effect of salt spray was evaluated on Loring Peach trees (*Prunus persica*) during the 1973-74 winter (Northover, 1987). The trees were located on the south side of an east-west section of the QEW, a busy, four-lane, controlled access highway near St. Catharines, Ontario.

The orchard was located at the same elevation as the highway. sodium and chloride tissue content of shoot tissue decreased with increasing distance from the highway. The chloride content of the peach twig tissue, from trees located 20 m from the highway, was greater than 4 times the levels found in trees 120 m from the highway (9,000 ppm as compared to 1900 ppm chloride). The sodium content was elevated more than 7 times the levels detected 120 m from the highway (6900 ppm as compared to 900 ppm sodium).

Fruit yield was reduced at distances less than 80 m from the highway and peach fruit number per shoot increased with increasing distance from the highway. Shoots in the tree canopy were 97% dead 20 m from the highway. Shoot death decreased with increasing distance from the highway, falling to 8% at 80 m from the highway and decreasing to a background level of less than 1% at 120 m from the highway. The sodium and chloride content of the shoots were positively correlated with the percentage of dead wood in the canopy of the trees.

The soil levels of sodium and chloride were not elevated on this site, indicating that the elevated tissue levels and plants effects were primarily due to aerial salt spray from the highway.

3.5.3.5 Salt Spray from a two-lane highway on blueberries in western Nova Scotia

Eaton *et al.* (n.d.) evaluated the effects of road salt from a two-lane highway, Highway 104, in the Folly Mountain area, west of Truro, over the winters from 1993 to 1995. Salt application in this area was 33 and 40 tonnes of sodium chloride per km of highway during the winters of 1993-94 and 1994-95, respectively.

They found that lowbush blueberry blossom number and yield was reduced within 35 m of the two-lane highway in western Nova Scotia and approached background levels beyond 50 m from the highway. Blossom number was reduced by 60% to 90% within 10 m of the highway and yield was reduced by 50% or more compared to samples taken at 50 m from the highway. Yield under protective structures of nursery film was 4224 kg/ha of fresh fruit in 1994 compared to less than 2000 kg/ha at 30 m and less than 200 kg/ha at 5 m from the highway. In 1995, yield under the protective structures was 8092 kg/ha compared to less than 3000 kg/ha at 35 m and less than 1500 kg/ha at 5 m from the highway.

Stem tissue salt levels taken under the protective structures were 0.53 and 0.3 g sodium chloride per 20 stems in 1993-4 and 1994-5, respectively. This compared to levels from 6 to over 10 g at 10 m from the road in spring 1994 and 3 to over 8 g in spring 1995. Tissue levels were elevated up to 45 or 50 m from the highway. Reductions in both blossom number and yield were negatively correlated with elevated salt content of the blueberry stems taken in winter and early spring.

3.5.3.6 Soil and woody plant concentrations adjacent to highways in interior British Columbia

Davis *et al.* (1992) reported on the causes of observed roadside tree injury and decline on 17 forested sites in south central/eastern British Columbia.

The sites were located on two, three or four-lane highways. At 15 of the sites, sodium chloride was used for winter maintenance at 60 to 130 kg/lane km as conditions dictate. On two of the sites that had gravel roads, sodium chloride was not used for de-icing, although sand with 3-5% sodium chloride was applied in the winter. In the summer, and calcium chloride or magnesium chloride was used for dust suppression, initially at 2 $L/m^2$, but currently at 1.6 $L/m^2$ in the summer.

The pattern of injury to conifer trees was similar between all the sites. Injury decreased with increasing distance from the highway. In most of the sites, the injury occurred on a narrow strip, within 15 m downslope of the highway. On one site, injury was evident for 40 m into a stand that received road runoff from a culvert. On another site, minor injury was evident 50 m from the highway due to wind and salt spray from the road.

Soil chloride concentrations at 0-10 cm depth in the control plots ranged from <1 to 12 ppm. Soil concentrations of chloride on the plots with plant injury ranged from 0.9 to 230

ppm chloride and were greater than 25 ppm on six of the sites. Two of the sites that were adjacent to a four-lane highway, had soil chloride levels ranging from 3.0 to 198 ppm.

Soil sodium concentrations at 0-10 cm depth in the control plots ranged from <1 to 8.5 ppm. Soil concentrations of sodium ranged from 0.02 to 50.2 ppm sodium on the plots with plant injury. At 13 sites, soil sodium concentrations were greater than the control on one or both of the injury plots and were greater than 17 ppm on seven of the sites. Two of the sites that were adjacent to a four-lane highway had soil sodium levels as high as 43 ppm.

The chloride content of the needles from the injury plots increased up to 3.4 times that found in the control needle samples. The sodium content of needles from the injury plots increased up to 206 times that found in the control needles.

Sodium tissue levels were not elevated on the two sites where sodium chloride is not used for winter de-icing. At these two sites, tissue chloride levels were 2 to 2.4 times greater than the control plots on at least one of the injury plots. The likely cause was the use of either calcium chloride or magnesium chloride for dust suppression as part of summer maintenance programs on these sites.

Based on plant injury symptoms, and sodium and chloride concentrations in soil and vegetation, salt was strongly implicated as a major contributor to the observed roadside tree injury and decline on 16 of the sites.

3.5.3.7 Soil and woody foliar concentration adjacent to a two-lane highway

Soilcon Laboratories Ltd. (1995) investigated the levels of salt in soil and plant tissue with respect to plant injury levels along a 2 km section of Loon Lake Road, a two-lane highway northwest of Kamloops in British Columbia. The dominant forest species on the site were ponderosa pine and Douglas-fir.

The individual rock salt applications rates were 22, 88 or 153 kg/two-lane km, depending on whether low, average or heavy applications were applied. The total salt loading over the winter was 1561 kg/two-lane km, consisting of 1031 kg applied as rock salt and 530 kg applied as sand with 5% salt. Salt or sand applications were made from November 15, 1993 to February 23, 1994.

Nine sites were evaluated within a 2 km section along Loon Lake Road, where trees displayed low, moderate or severe salt injury symptoms. Trees that fell in the moderate and severe injury classes were located from 3 to 8.4 m from the road. In comparison, trees that fell in the low injury class were located 10 to 20 m from the road.

Soil concentrations of chloride and sodium were sampled on the nine sites in December 1993 and April 1994 and compared to control values sampled in April 1991. On sites with moderate and severe tree injury, soil concentrations of chloride measured in the 0-10 cm layer were 31.3 ppm chloride (range of 84.5-4.1) in December. By April, the concentrations fell to 5.12 ppm chloride (range of 12.6 -1.6). On sites with low tree injury, soil concentrations of chloride measured in the 0-10 cm layer were 7.2 ppm chloride (range of 23.5-1.4) in December. By April, the concentrations fell to 2.9 ppm chloride (range of 4.5-1.3). This compared to background levels of 3.8 ppm chloride (range 7.5-0.2).

On sites with moderate and severe tree injury, soil concentrations of sodium measured in the 0-10 cm layer were 15.9 ppm sodium (range of 28.2-1.9) in December. By April, the concentrations fell to 9.1 ppm sodium (range of 30.7-1.0). On sites with low tree injury, soil concentrations of sodium measured in the 0-10 cm layer were 4.7 ppm sodium (range of 11.7-5.6) in December. By April, the concentrations fell to 1.2 ppm sodium (range of 1.8-0.5). This compared to background levels of 2.3 ppm sodium (range of 2.7-2.0).

Soil concentrations of chloride and sodium were higher on the sites with plants in the moderate and severe injury class, than on the sites with plant in the low injury class in both December and April. Soil concentrations were approaching background levels by the April sampling period. It was likely that sodium and chloride had leached from the soil by April by rainfall since the last salt application was in February.

Over the December to May sampling period, foliar chloride concentrations ranged from 110 to 560 ppm in trees in the low injury class, from 110 to 3180 ppm in trees in the moderate injury class and from 870 to 5590 ppm in trees in the severe injury class.

During the same period, foliar sodium concentrations ranged from 0.5 to 70 ppm in trees in the low injury class, from 0.5 to 190 ppm in trees in the moderate injury class and from 30 to 920 ppm in trees in the severe injury class.

3.5.3.8 Woody foliar concentrations directly adjacent to a two-lane highway

Button and Peaslee (1966) reported foliar concentrations of chloride and sodium in mature (about 70 year old) sugar maple (*Acer saccharum*) leaves. The trees were growing close (from 1-4 m) to Route 17 between Middletown and Durham, a two lane highway in Connecticut. The research is relevant to Canadian conditions since sugar maple is a native forest species, used for maple syrup production and planted as a landscape tree.

The trees growing on the west side of the highway (positive distance values) had road surface drainage flowing directly towards the trees. The trees growing on the east side of the highway had drainage diverted by a curb that had been installed during the summer prior to the study. Foliar concentrations of chloride at the different sampling periods averaged 5200 to

6700 ppm on the west side of the road. These were significantly higher than the concentrations found on the east side of the road, averaging 1600 to 5400 ppm. This compared to levels ranging from 200 to 1400 ppm chloride in control trees of the same species and age, located away from a road. Foliar sodium levels ranged from an average of 1100 to 1600 ppm on the west side of the highway compared to non-detectable to 200 ppm on the east side of the highway, and 0 in the control trees.

The higher concentrations of chloride and sodium found in the foliage of the trees on the west side of the highway with overland surface flow were correlated with moderate to severe injury symptoms in the trees on the west side of the road. This compared to no or light injury symptoms in the trees on the east side of the road and no injury in the control plants.

3.5.3.9 Soil and woody plant concentrations down-slope from a four-lane highway, British Columbia

A site investigation was conducted in 1989 to investigate the sources of tree injury and decline that was evident in Boitanio Park, located in Williams Lake, British Columbia (Van Barneveld and Louie, 1990).

Boitanio Park is located west of a four-lane section of Highway 97 and the area of concern slopes toward the southwest with a grade of 5 to 15%. Two culverts were located along the highway above the park. The dominant tree species in the park was rocky mountain Douglas-fir (*Pseudotsuga menziesii* var. *glauca*).

Plant injury was evaluated along a grid pattern running away from the highway with sampling locations every 50 m along the grid. Trees in the low injury class had less than 10% discoloration and dead branches with healthy leaders. Trees in the moderate injury class had 10 to 50% discolouration; defoliation and some dead branches with leaders alive. Trees in the severe injury class were dead or had greater than 50% foliar discolouration; defoliation and dead tops.

In general, the sites with trees in the severe injury class were on the east side of the park, within 50 m of Highway 97. Tree injury decreased with increasing distance from the highway. The sites with trees in the low injury class were generally located from 75 to 100 m away from the road.

Soil concentrations of sodium and chloride were elevated on sites with severe or moderate injury compared to those with low injury. The average soil concentration of sodium was 108.7 ppm on the severe injury sites, 37.9 ppm on the moderate injury sites and 29.0 ppm on the low injury sites. The average soil concentration of chloride was 52.1 ppm on the severe injury sites, 50.0 ppm on the moderate injury sites and 20.3 ppm on the low injury sites. Severe injury sites had soil sodium concentrations that were 3.7 times the concentration in low injury

sites, further away from the highway. Similarly, severe injury sites had soil chloride concentrations that were 2.6 times the concentration in low injury sites.

Foliar concentrations of sodium and chloride were higher in the plants with a severe or moderate injury rating compared to the plants with a low injury rating. The average concentration of sodium in the 0 to 3 year needles was 113 ppm on the severe injury sites, 54.8 ppm on the moderate injury sites and 59.7 ppm on the low injury sites. This compared to average concentrations of sodium in the 4 to 6 year needles of 208 ppm on the severe injury sites, 72.7 ppm on the moderate injury sites and 47.9 ppm on the low injury sites.

The average concentration of chloride in the 0 to 3 year needles was 3560 ppm on the severe injury sites, 2630 ppm on the moderate injury sites and 572 ppm on the low injury sites. A similar pattern was observed in the average concentrations of chloride in the 4-6 year needles: 4180 ppm on the severe injury sites, 2667 ppm on the moderate injury sites and 1060 ppm on the low injury sites. Foliar concentrations of sodium and chloride decreased with increasing distance from the highway.

Other factors such as recent drought, presence of other contaminants in the run-off, insects and recent brush removal may have aggravated the decline of the trees. However it was determined that these factors were not the primary cause of the decline in the park. The injury symptoms on the Douglas-fir in this site were consistent with salt injury and supported by the pattern of decreasing injury symptoms with increasing distance from the road. Elevated soil and tissue concentrations of sodium and chloride were correlated with more severe injury symptoms in the trees.

3.5.3.10 Soil and woody foliar concentrations adjacent to a patrol yard

Racette and Griffin (1989) reported on the investigation of the cause of severe woody plant injury in the vicinity of a highway maintenance patrol yard, east of Kenora, Ontario.

Trees in the area behind the sand dome and salt storage sheds and along a drainage channel that received drainage from the highway and patrol yard area had severe injury symptoms.

In a nearby sand and gravel storage area, salt-treated sand had been stored on at least one occasion. In this area, jack pine, spruce, balsam fir and poplar trees had died a number of years before. Existing vegetation was damaged along a drainage course in this area. Grasses had been killed and trembling aspen had symptoms of severe marginal necrosis.

Plant tissue levels of sodium and chloride were sampled in September 1988, in the areas where the injury was evident. Foliar concentrations of chloride ranged from 1800 ppm (serviceberry foliage) to 22 000 ppm chloride (white birch foliage). Foliar concentrations of

sodium ranged from 10 ppm (black spruce foliage) to 86 ppm sodium (serviceberry foliage). Background foliar concentrations of chloride ranged from less than 20 ppm (serviceberry and white birch) to 1900 ppm chloride (trembling aspen). Background foliar concentrations of sodium ranged from 7 ppm (black spruce) to 19 ppm sodium (serviceberry).

Twig concentrations of sodium and chloride were also elevated in these areas. Twig concentrations of chloride ranged from 900 ppm (trembling aspen) to 9100 ppm chloride (black spruce). Twig concentrations of sodium ranged from 9 ppm (trembling aspen) to 78 ppm sodium (black spruce). Background twig concentrations of chloride ranged from less than 20 ppm (trembling aspen) to 200 ppm chloride (black spruce). Background twig concentrations of sodium ranged from 7 ppm to 17 ppm sodium (both in black spruce).

Surface soil concentrations of sodium and chloride at these two sites, taken at 0 to 5 cm depth, were elevated compared to a control site, remote from the area. The soil concentration of chloride ranged from 780 to 1200 ppm and the soil concentration of sodium ranged from 370 to 680 ppm. Background concentrations were 15 ppm chloride and 91 ppm sodium.

Changes were initiated in the winter of 1988-89 to reduce losses of salt from the patrol yard operations. The area and severity of the vegetation injury had decreased by August 1989. The concentrations of sodium and chloride in the foliage also declined, although levels were still elevated in comparison to the control.

### *3.5.4 Risk assessment summary and conclusions*

Sodium chloride, applied as a de-icer, can have a harmful effect on plants growing along roads or in areas that have localized contamination due to runoff with elevated salt levels. Elevated soil levels of sodium and chloride or aerial dispersion of sodium and chloride result in severe reductions in flowering and fruiting of sensitive plant species; severe foliar, shoot and root injury; growth reductions; and reductions in germination and seedling establishment. The species affected include native grass species; wetland species such as sphagnum moss and sedges; and woody species such as maple, pine, Douglas-fir, dogwood, peach and plum.

Severe effects may result in plant mortality, while repeated (chronic) exposure of perennial plants to elevated salt levels, year after year, results in reduced plant growth and death of shoot and leaf tissue. Repeated stress on plants reduces plant vigour and the ability to deal with insects, disease and abiotic stresses. These effects can lead to loss of plants within a community as well as impacts on other organisms that rely on plants for food and cover.

Changes in plant communities in response to elevated levels of de-icing salts, have been recorded in areas impacted by road salt run-off and aerial dispersion. Halophytic species, such as cattails and common reed grass, readily invade areas impacted by salt, leading to the changes in occurrence and diversity of salt-sensitive species. The composition of non-salt tolerant

communities changes due to the loss of sensitive species and replacement by salt-tolerant species.

The zone of impact is usually linear, along roads and highways or other areas where sodium chloride is applied for de-icing. Aerial dispersal of sodium chloride occurs along roads during the winter months when de-icing is required and impacts mainly woody plants. The impact of aerial dispersion of sodium chloride extends up to about 80 m from the edge of multi-lane highways and up to about 35 m of two-lane highways where de-icing salt is used. The degree and distance of dispersion depends on the salt load, traffic volume and velocity, local topography and prevailing winds.

Impacts of road salts on forest species adjacent to roadsides have been documented in central and southern British Columbia. In these areas, the zone of impact was in the first 10 to 15 m from two-lane highways. Adjacent to a four-lane highway in British Columbia, the zone of severe injury of forest trees covered the first 50 m from the highway. Areas of high forest density in Canada that experience medium to high salt loadings (based on average annual loadings, by maintenance district) include Vancouver Island, southwestern and central Alberta, central Ontario and parts of southern Ontario, southern and central Quebec and areas in New Brunswick and Nova Scotia. Fifty-three percent of the primary species of forest trees in Canada have been rated as sensitive to road salt.

Fruit crops experience severe plant injury and reduced fruit production in a zone up to 50 to 80 m from four-lane highways in southern Ontario and about 35 m from two-lane highways in Nova Scotia. Sixty-five percent of 32 cultivars or varieties of fruit trees, vines or shrubs have been rated as sensitive to salt.

Sensitive landscape plantings and nursery crops suffer severe plant injury and plant death due to elevated soil levels of road salt and salt spray. From 30 to 40% of common landscape species used in Canada and Ontario roadside woody species have been rated as sensitive to road salts.

## 3.6 Wildlife

### *3.6.1 Exposure characterization*

Sodium is an indispensable component of the physiological processes of all vertebrates but is toxic when taken in excess. Typically, surplus sodium is removed by an increase in glomerular filtration rate and a decrease in the percentage of sodium reabsorbed by the kidneys. Terrestrial birds, especially herbivorous and granivorous species, are more likely to be salt deficient and are poorly equipped to deal with excess sodium. Any animal attempting to satisfy a "salt hunger" generally overshoots its deficit by a substantial amount, and the increase persists for some time after the deficit is replaced (Schulkin, 1991). Over-consumption of salt is in turn regulated via a

feedback mechanism: the thirst response. The absence of a source of water therefore increases the toxicity of ingested salt (see Section 2.6.2.1). Sodium-deficient wildlife are known to travel great distances to obtain and ingest salt and to visit roads where salt has been applied (Schulkin, 1991). One concern raised by this assessment is that the "footprint" of a salted road may be quite large when highly mobile wildlife species are attracted from great distances.

#### 3.6.1.1 Mammals

The most visible interaction between road salt and wildlife concerns the large ungulates, such as moose (*Alces alces*), mule deer (*Odocoileus hemionus*), white-tailed deer (*Odocoileus virginianus*), elk (*Cervus canadensis*) and bighorn sheep (*Ovis canadensis*). Road salt attraction has been identified as a main reason for kills of bighorn sheep and a minor reason for kills of elk in Jasper National Park (Bradford, 1988). In May and July, pools of salty snow melt along the roadsides are considered a major cause of moose–vehicle accidents in Northern Ontario (Fraser and Thomas, 1982) and Quebec (Jolicoeur and Crete, 1994). The role that road salt could play in the mortality of other wildlife species such as small mammals commonly killed by traffic is not known.

#### 3.6.1.2 Birds

Twelve published reports of bird kills associated with salted roads were identified. Two incidents were formally diagnosed as salt poisoning (Trainer and Karstad, 1960; Martineau and Lair, 1995) and observations of potentially aberrant behaviour suggestive of toxicosis were made in several other cases. sodium chloride was usually identified as the substance to which birds were exposed, although in one case the road salt applied was calcium chloride (Meade, 1942). Geographically, these kills occurred at several sites within the Canadian and U.S. snow belt from 1942 to 1999. One report originated from Germany. At least two reported kills were large, involving more than a thousand birds each. Given the difficulty of finding avian carcasses (Mineau and Collins, 1988), the high rate of scavenging reported from sites where birds are routinely killed at roadside (John Woods, Parks Canada, personal communication; Craig W. Benkman, New Mexico State University, personal communication) and the low rate of reporting for wildlife mortality events in general, the number of reports of bird mortality associated with the use of road salt is significant and suggests that kills are probably more widespread and frequent than indicated by documented reports alone. Supporting this view is the fact that other researchers and biologists, when contacted, were very familiar with kills of birds on salted highways even though their observations had not been published. In one location (Mount Revelstoke Park), mortality of siskins and other winter finches (see below) has been seen frequently enough over the last 25 years that they are called "*grill birds*" by the local inhabitants, in reference to their propensity to be collected by the front end of moving vehicles (John Woods, Parks Canada, personal communication). The kills often occur in sections of the highway with curves or where there are many cracks and crevasses in the pavement where salt can accumulate, although they may occur anywhere the roads have been sanded and salted. Baker (1965) stated that the inhabitants of one Maine community "*looked upon this bird*

*slaughter as a natural and everyday occurrence.*" Another researcher reported seeing "*hundreds of dead crossbills that were hit by vehicles while on the road eating salt*" (Craig W. Benkman, New Mexico State University, personal communication).

Cardueline finches (Family *Fringillidae*, subfamily *Carduelinae*: crossbills, grosbeaks and siskins) were involved in 11 out of 12 published incidents. All cardueline finches are protected species listed under the *Migratory Bird Convention Act*. This group of seed-eating birds ranges throughout the boreal forest, moving to more southern latitudes only when seed yield is low. Although they will eat deciduous seed, insects and berries, their primary diet, particularly in the winter, consists of coniferous seeds. Their attraction to salt is well known. Red crossbills (*Loxia curvirostra*) have been trapped using salt as bait (Dawson *et al.*, 1965), and cardueline finches were found to prefer sodium over other minerals regardless of grit size (Bennetts and Hutto, 1985).

The information from reported kills and the behavioural/social characteristics of the cardueline finches suggest that this may be the group most at risk of acute salt toxicity from ingesting road salt. However, because the birds tend to travel and forage in large flocks in the winter, there is undoubtedly a bias for a higher detectability and reporting of kills. Trainer and Karstad (1960) reported Bobwhite quail (*Colinus virginianus*), Ring-necked pheasant (*Phasianus colchicus*) and feral dove (*Columba livia*) as well as Eastern cottontails being poisoned.

It is often assumed that salt is ingested in order to fulfil a physiological need associated with a largely vegetarian diet. However, the taking of salt crystals as grit cannot be ruled out. Grit is used to aid in the grinding of food and to provide supplementary minerals to bird species with low calcium diets (Gionfriddo and Best, 1995). Across species, grit size preferences are linearly related to bird size. The size of salt particles from a salt mine in Ontario ranged from 0.6 to 9.5 mm (Canadian Salt Company Limited, 1991). Because salt particles applied to roads undergo a gradual size reduction as they melt (Art Letts, Morton Salt, personal communication), salt particles overlap broadly with the preferred grit size for any-sized bird from the time of application to some undetermined time after application. The large variation in the starting size of road salt particles ensures that a suitable size of grit will be available for an extended period.

### *3.6.2 Effects characterization*

#### 3.6.2.1 Acute toxicity of sodium chloride

Incidents of vertebrate salt toxicity in domestic or captive stock fall under several main categories: accidental overdose in feed beyond a level that can be compensated by drinking more water (Sandals, 1978; Swayne *et al.*, 1986; Howell and Grumbrell, 1992; Wages *et al.*, 1995; Khanna *et al.*, 1997); exposure to saline drinking water (Franson *et al.*, 1981), saline lakes (Windingstad *et al.*, 1987; Meteyer *et al.*, 1997), or the provision of salt supplements with deprivation of water (Trueman and Clague, 1978; Scarratt *et al.*, 1985). Reports of salt

toxicosis in free-ranging vertebrate wildlife have been the result of exposure to road salt, drought, ice, hypersaline lakes and discharge ponds from various industries (Baeten and Dein, 1996).

Rats have an oral $LD_{50}$ of 3000 mg/kg, and mice an $LD_{50}$ of 4000 mg/kg (Bertram, 1997). Sodium chloride administered as a saturated water solution (approximately 2100 mg/kg) usually resulted in death within 24 hours (Trainer and Karstad, 1960). Repeated small doses of salt produced no illness if water was not restricted.

The Canadian Cooperative Wildlife Health Centre in Saskatoon and the National Wildlife Research Centre, Environment Canada recently conducted a joint study on the acute effects of salt on wild caught House sparrows (*Passer domesticus*) (Wickstrom *et al.*, in prep.). The "up-and-down" method (OECD, 1998) was used in a pilot study to estimate the approximate lethal oral dose of granular sodium chloride in birds that were non-fasted but without access to water for 6 hours post dose. Results indicated an approximate $LD_{50}$ of 3000 to 3500 mg/kg, which is similar to the rodent values. A tentative no-effect level (mortality) was estimated to be 2000 mg/kg in this pilot study, although mortality was seen at 1500 mg/kg in the subsequent phase of the study.

3.6.2.2 Sub-lethal effects of excess salt ingestion in birds and mammals

Several authors reporting wildlife incidents associated with road salt made note of behavioural deficits in exposed birds. The most common observation is that the birds appeared unusually fearless and could be approached easily (Meade, 1942; Trainer and Karstad, 1960; Baker, 1965; Thiel, 1980; Smith, 1981; Woods, personal communication, 1999). Others described the birds as "*weak and slow*" (Martineau and Lair, 1995) or appearing sick (Meade, 1942). Trainor and Karstad (1960) reported "*depression, tremors, torticollis, retropulsion, and partial paralysis*" for birds and mammals affected in one incident.

These signs are closely matched by observations made in the course of laboratory studies. Pheasants fed increased amounts of sodium in their mash exhibited signs of intoxication when the drinking water was restricted. These included depression, followed by excitement, tremors, torticollis, opisthotonos, retropulsion, complete incoordination and coma (Trainer and Karstad, 1960).[1] Not all signs were seen in the same animal. Frequent signs reported in poultry and in swine include salivation, diarrhea, a staggering gait, muscular spasms, twitching and prostration (Humphreys, 1978). In Wickstrom *et al.* (in prep.), following the pilot study reported above, House sparrows were dosed orally with granular sodium chloride at 0, 500, 1500, 2500 or 3500 mg/kg. Overt clinical signs were observed at 1500 mg/kg or higher and

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[1] Depression: General lethargy
Torticollis: Abnormal head carriage and straining of the neck
Opisthotonos: Arching of back and arching of neck over back
Retropulsion: Spasmodic pushing out with the legs

included rapid onset (< 30 min) of depression, ataxia and inability to fly or perch, with death in as little as 45 minutes. Birds which survived for 6 hours usually recovered. Plasma sodium concentrations > 200 mMol/L were consistently associated with overt clinical signs. Lesions in the form of gizzard edema were observed after 1 hour in most birds dosed with 500 mg/kg or higher, and brain stem vacuolation, also consistent with edema, was seen in some birds showing clinical signs.

There is no record of moose or deer suffering from salt toxicosis. However, when moose are drinking salty water, they tend to lose their fear of humans and vehicles (Jones *et al.*, 1992) in contrast to moose not drinking salty water that move away from approaching humans. The only documented case of small mammals exhibiting signs of salt toxicosis is Eastern cottontail rabbits (*Sylvilagus floridanus*) reported during a severe winter in Wisconsin (Trainer and Karstad, 1960).

### *3.6.3 Risk characterization*

Because mortality has been documented and is thought to be much more frequent and widespread than is reflected by the published record, the risk to cardueline finches and perhaps other bird species is likely significant. Locally, the risk to large mammals may also be high. The main uncertainty associated with this risk analysis is the extent to which salt toxicity contributes to vehicle collisions. Also, if salt toxicity is occurring, it is relevant to ask whether wildlife, cardueline finches in particular, could be killed by salt ingestion even in the absence of a vehicle strike.

#### 3.6.3.1 Estimating the contribution of salt toxicity to vehicle strikes

The severe behavioural impairments (depression, tremors, torticollis, retropulsion and partial paralysis) observed at one site, as well as the finding of elevated brain sodium level at another, argue strongly for a contributory role of salt toxicity to roadside bird kills. The more common observation of unusual fearlessness documented in both birds and mammals could be an early symptom of intoxication or it could be the manifestation of animals under extreme salt hunger modifying their usual behaviour toward potential danger.

Although overt signs of intoxication were seen in the House sparrow at 1500 mg/kg and higher, the level of dosing at which a more subtle behavioural impairment could be manifest is not known. A lower limit for potential impairment, using the House sparrow as a model, can be estimated as follows:

The distribution of normal sodium values in the plasma of the sparrows is very narrow (mean of 163.2 mMol/L, range of 158–168, n=12). The assumption is that adverse effects (such as reduced coordination and weakness) may begin when sodium homeostasis is breached and elevated sodium levels are being delivered to target organs. This level in the House sparrow model was determined to be 266 mg/kg body weight.

For this analysis, we assume that salt crystals are most likely to be picked up whole as are grit particles. A finch trying to satisfy a salt hunger might pick up a granule of a size that it is "comfortable" with. The maximum recorded size for grit in the House sparrow is 2.4 mm (Gionfriddo and Best, 1995). This allows one to estimate the number of particles that need to be ingested by birds in order to attain specific CTVs (Table 22).

This calculation suggests that birds could be sub-lethally impaired following ingestion of a single salt particle and could be killed by as few as two particles.

The average size of grit ingested by the House sparrow was 0.5 mm (Gionfriddo and Best, 1995). Assuming birds were intent on picking up salt particles of this "preferred" size for digestion, the above calculations were repeated for average-sized grit. In fact, this average grit size is likely an underestimate because it is based on "worn" grit extracted from sparrow gizzards. The average also encompasses very fine mineral particles which were probably ingested accidentally along with food. These results are given in Table 23.

Although the number of particles that need to be ingested to reach CTVs is much higher than that calculated in Table 22, this number of particles can easily be ingested if compared to average grit counts. Therefore, birds in need of replenishing their grit supply may easily achieve doses that would be toxicologically relevant.

#### 3.6.3.2 Conclusions and discussion of uncertainty

Road salt increases the vulnerability of birds to car strike and may poison some birds directly. It is clear that, even without road salt, some birds would be coming to highways for grit, and possibly clays. The relative contribution of road salt as an attractant is impossible to estimate for songbirds, although road salt is thought to be the primary attractant for mammals. What differentiates road salt from, for example, sand which is also used on highways, is the impairment and possible poisoning of exposed birds by the salt.

It is not known if the House sparrow is a suitable toxicological model for cardueline finches and other native birds. The House sparrow has middle-eastern origins and may therefore be genetically predisposed to be more salt tolerant than cardueline finches. On the other hand, consumption rates of grit may be high in House sparrows relative to other bird species (Gionfriddo and Best, 1995). The scenarios presented above assumed a consumption of salt based on grit need (Table 22) as well as on optimizing salt intake Table 23. Regardless of the exact particle size taken, salt-deprived birds could ingest very large quantities before feedback mechanisms reduce the desire for salt.

It is likely that birds will be at higher risk of salt toxicosis when water availability is reduced during severe winters (Trainer and Karstad, 1960). Birds have been observed eating snow, catching snowflakes during a storm, and chipping ice to obtain water (Wolfe, 1996).

Oeser (1977) reported that crossbills were eating snow in the reported German kill incident. There could be negative energetic consequences of snow ingestion in response to salt over-consumption. Melted snow on the roads may be the most obtainable source of water. Depending on the concentration of salt in the snow melt, consumption of such water may increase salt ingestion rather than alleviating salt toxicosis.

The overlap between the distribution of winter finches and the Canadian road system receiving road salt was determined to be extensive when mapped by Brownlee *et al.* (2000). The data needed to assess kill frequency (whether fatal attraction, toxicosis-induced car strikes or lethal ingestion) is not available. Also, the length of time the applied salt is retained on or near the road surface (e.g., in the soil), where it could create an artificial "lick" attractive to both birds and mammals even after granules have disappeared, is difficult to assess.

A further aspect not covered by this assessment is the indirect effects of road salts on wildlife. Under some conditions, especially where habitat may be limiting, road verges can be valuable, both as breeding habitat for wildlife and also as a corridor between suitable habitat patches (e.g., Oetting and Cassell, 1971; Drake and Kirchner, 1987; Bennett, 1991; Camp and Best, 1993a,b). Efforts are currently under way in several jurisdictions to improve roadside management in order to increase the value of this habitat. Road salts can have an adverse effect on terrestrial plants (Section 2.5). A reduction in plant cover or community shift could affect wildlife that depend on these plants for food or shelter.

Despite these remaining uncertainties, the importance of wildlife kills and the contribution of road salt to this mortality have probably been underestimated by wildlife managers and transport officials.

## 3.7 Ferrocyanides

This section is based on a detailed review of ferrocyanides presented by Letts (2000).

### *3.7.1 Exposure characterization*

Sodium ferrocyanide dissolves in water to release the stable ferrocyanide anion which is not volatile and resists further break-up unless illuminated. The anion is fairly mobile in groundwater but reacts readily with iron to form the precipitate ferric ferrocyanide, a very stable, non-toxic, relatively immobile compound which is a major removal pathway of ferrocyanide from groundwater. Under favourable conditions, including non-illumination, the half-life of ferrocyanide is approximately 2.5 years (Higgs, 1992) while that of ferric ferrocyanide can extend to a thousand years (Meeussen *et al.*, 1992a).

Two characteristics of the ferrocyanide anion are paramount. It is virtually non-toxic in the complexed form (Rader *et al.*, 1993) but in solution under direct light it photodecomposes,

liberating free cyanide which rapidly reacts to produce the highly toxic and volatile HCN. Outside of solution, photolysis of ferrocyanide is slight (American Cyanamid Company, 1953).

Photolysis of the ferrocyanide anion is a well-studied phenomenon (Broderius, 1973a; Broderius and Smith, 1980; Otake *et al.*, 1982; Clark *et al.*, 1984; Meeussen *et al.*, 1992a). It can liberate as many as five of the six $CN^-$ associated with the parent compound. The reaction is a function of the initial concentration, intensity of illumination, pH and temperature among other factors.

Free cyanide in the environment is subject to a number of attenuation processes. It is readily chelated with numerous transition metals to form more stable, less toxic materials (Chatwin, 1990). The presence of clay or organic matter removes free cyanide by surface adsorption (Theis and West, 1986). Additionally, it is oxidized to the relatively innocuous cyanates and thiocyanates in the presence of sulphur.

Soil

*Non-illuminated ferrocyanide:* The largest portion of research covering the behaviour of non-illuminated ferrocyanides in soil has focussed on waste compounds from former manufactured gas plant (MGP) sites. Studies at such sites indicate that the presence of ferrocyanide is tightly restricted around the source site (Effenberger, 1964; Parker and Mather, 1979). This low mobility is apparently due to the presence of sulphur and transition metals in the soil. Iron under pH conditions of about 4 to 7 combines with the ferrocyanide anion to produce the sparingly soluble ferric ferrocyanides known as prussian blue (Meeussen *et al.*, 1992b). This compound is evident in the blue colouration of the soil at many abandoned MPG sites. In alkaline soils (pH above 7), ferrocyanide in solution retains the anion form and is fairly mobile. It has been noted that under strongly acidic conditions ferrocyanide anions dissociate to release $CN^-$ (D.A. Belluck, personal communication). It has been suggested that the appropriate conditions may occur in the laboratory but seldom or never in the environment (Chatwin, 1990).

Retention and immobilization in soils in low toxicity forms is the major attenuation pathway limiting the potential toxic effects of ferrocyanide. Particle adsorption in clay-bearing moderate pH soils may effectively contain ferrocyanide anions. Geotite (a-FeOOH), a common surface coating of soil particles, removes as much as 95% of the ferrocyanide anion through adsorption at pH 4 (Theis and West, 1986). These removal methods are abetted by moderate pH levels. Soils in Canada are mildly acidic in the forested regions of eastern Canada, an area of heavy salting activity and are alkaline in the Prairies (Paul Arp, personal communication, 2000). Immobilized ferrocyanide is also subject to chemical conversion to non-toxic compounds in the presence of sulphur and microorganisms which degrade metal complexed cyanides have been identified (Mudder, 1991).

*Illuminated ferrocyanide:* Photolysis of ferrocyanide under illumination is a complex, intensely studied reaction (Broderius, 1973a; Broderius and Smith, 1980; Otake *et al.*, 1982;

Clark *et al.*, 1984; Meeussen *et al.*, 1992a). Factors affecting the process include pH, temperature, initial concentration, season and time of day. In their study of photolytic reactions, Miller *et al.* (1989) reported that free cyanide release is restricted to a soil depth of 1 mm. This suggests that only ferrocyanide anions within the top 1 mm of soil are subject to the process.

Hydrogen cyanide produced within the soil is only mildly persistent. It has an estimated half life of four weeks to six months (Howard *et al.*, 1991). It is adsorbed at the rates of 0.05 mg/g by clays and 0.5 mg/g by organic matter (Chatwin, 1989). It is also subject to hydrolyzation to formic acid up to a rate of 4% in saturated soils (Chatwin, 1990). Volatilization of HCN from soils accounts for as much as 10% of losses but saturation of the soil retards this process by a factor of $10^4$ (Chatwin, 1990). Biological degradation of various cyanides by soil microbes (Towill *et al.*, 1978; Dubey and Holmes, 1995) or assimilation by plants (Fuller, 1984; Knowles and Bunch, 1986) is an efficient removal system which is strongly diminished under saturated anaerobic conditions (Strobel, 1967).

Water

Ferrocyanide dissociates very slowly under non-illumination. Under this condition the amount of free cyanide released from concentrations of ferrocyanide in the range of 1 to 100 000 mg/L vary from 1.2 to 6.1 µg/L. However, under environmental, illuminated conditions rapid conversion of ferrocyanide to free cyanide has been reported (Ferguson, 1985; Singleton, 1986).

In water, free cyanide is converted to hydrogen cyanide, a weak acid, through the equilibrium reaction $H^+ + CN^- \leftrightarrow HCN$. The HCN state is highly favoured under pH values of 6. HCN is highly volatile and, under environmental conditions, quickly dissipates from water bodies, volatilization rate being a function of concentration, temperature, pH and water flow rate (Schmidt *et al.*, 1981; Melis *et al.*, 1987). Secondary cyanide removal processes include complexation and precipitation, biological degradation, adsorption by organic material and uptake by plants. A number of naturally occurring organisms are known to produce cyanides (Knowles, 1976).

Air

Ferrocyanide itself does not volatilize. HCN is highly volatile but is expected to readily dissipate to harmless levels in the atmosphere with an estimated half-life of 89 days to 2.4 years (Howard *et al.*, 1991).

Biomagnification

Towill *et al.* (1978) found no studies reporting biomagnification of cyanide.

### *3.7.2 Measured and estimated environmental concentrations*

Reported cyanide concentrations measured in runoff waters range from 2.3 to 22 µg/L for free cyanide and from 3 to 270 µg/L for total cyanide (Hsu, 1984; Ohno, 1989a; Novotny *et al.*, 1997; Mayer *et al.*, 1998). Since actual data are limited, estimations concentrations were also derived.

Morin and Perchanok (2000) documented road salting activity in Canada. The highest level of use in Canada is 10 150 g salt/$m^2$ and the highest addition rate of sodium ferrocyanide to road salt is reported to be 124 mg/kg (Letts, 2000b). This corresponds to 86 mg $Fe(CN)_6^{-4}$ / kg or a stoichiometric $CN^-$ content of 63.7 mg/kg. From these values, the distribution rate is calculated as being 877.8 mg $Fe(CN)_6^{-4}$ / $m^2$ or 646.6 mg $CN^-$/ $m^2$. Using annual precipitation data, the concentration range of $Fe(CN)_6^{-4}$ in runoff water can be determined to be 0.000142 to 1.42 mg/L which corresponds to a stoichiometric content of 0.000104 to 1.04 mg $CN^-$/L.

In soils, since local conditions will dictate the mobility of the ferrocyanide, two sets of assumptions are proposed. Under Case I, ferrocyanide is precipitated out of solution and the annual application is retained in the upper 2 cm of soil. Under Case II, ferrocyanide remains in solution and 20% of the annual application is retained in the first 20 cm of soil. For Case I, the resultant soil concentration ranges from 0.0043 to 43.8 mg $Fe(CN)_6^{-4}$/kg soil which corresponds to a stoichiometric $CN^-$ content of 0.0032 to 32.3 mg/kg soil. Under Case II, it ranges from 0.000086 to 0.88 mg $Fe(CN)_6^{-4}$ /kg soil which corresponds to a stoichiometric $CN^-$ content of 0.000064 to 0.64 mg/kg soil.

### *3.7.3 Effects characterization*

Initial assessment suggests that the greatest inherent danger in the use of sodium ferrocyanide lies with the ability of the ferrocyanide anion to photodecompose resulting in free cyanide. Therefore, the following sections summarize the known effects of both these compounds on terrestrial and aquatic biota. The limitations of determining toxicity under artificial laboratory conditions must be taken into account.

Aquatic biota

The main factors affecting toxicity in water are concentration and water temperature. Toxicity is also modified by the level of dissolved oxygen and salinity. The literature contains a number of comprehensive reviews on the toxicity of cyanide to freshwater organisms (Doudoroff, 1966; Doudoroff, 1976, 1980; Leduc *et al.*, 1982; US EPA, 1985a). Some organisms display reversible acclimatization to the toxic effects.

*Aquatic Microorganisms:* The effects of cyanide are quite diverse among various microbial species. Many species exhibit remarkable resistance to noxious effects and, indeed,

some species are employed in cyanide detoxification processes (Chatwin, 1990; Fallon *et al.*, 1991). On the other hand, adverse effects to *Pseudomonas putida* have been reported at the **1 µg/L** level (US EPA,1985a). This is the lowest concentration at which adverse effects on aquatic microorganisms have been reported (Letts, 2000a).

*Aquatic Plants:* Toxicity data on this group is scarce. However, toxic effects to plants are unlikely at levels known to adversely affect invertebrates (US EPA, 1980). The most sensitive species, *Scenedesmus quadricauda*, exhibits incipient cell inhibition under a 96-hour exposure to **31 µg/L** free cyanide (US EPA, 1985a).

*Aquatic Invertebrates*: In this group, onset of ferrocyanide toxicity generally exceeds 1000 µg/L. On the other hand, the lowest free cyanide 96-h $LC_{50}$ reported in the literature is **83 µg/L** for *Daphnia magna* (US EPA, 1985a; Eisler, 1991). Divergent sensitivity in mixed sub-species groups may cause a population structure shift following exposure in some communities (Smith *et al.*, 1979). For additional data, see Letts (2000).

*Aquatic Vertebrates*: This group has been intensely studied, for example, by Leduc *et al.* (1982). They are less sensitive to ferrocyanide (Schraufnagel, 1965) than to free cyanide (Leduc *et al.*, 1982). Fish as a group appear more sensitive to free cyanide than invertebrates. The 96-h $LC_{50}$ estimates lie in the range of 40 to 200 µg HCN/L (US EPA, 1985a). A wide variety of physiological and behavioural effects has been reported. Life stage investigation suggests the juvenile phase is most sensitive with a negative impact on growth commonly reported. Adverse effects on predation and avoidance behaviours and swimming ability have been reported. Adverse reproductive effects have been selected as a toxicity target indicator. Schraufnagel (1965) and Smith *et al.* (1979) found spawning to be inhibited at concentrations of **5.0 and 5.2 µg/L**, respectively.

Terrestrial Biota

The primary effect of cyanide is an interference with respiration as a result of disruption of a mitochondrial enzyme (Towill *et al.*, 1978; Way *et al.*, 1988). If the effect is not rapidly fatal, recovery is generally quick.

*Terrestrial microorganisms:* The organisms in this group show few adverse effects as a result of cyanide exposure. Some show such adaptations as alternate respiratory pathways. Evidence suggests the existence of a "cyanide microcycle" enabling microorganisms and plants to use HCN as a source of nitrogen and carbon (Allen and Strobel, 1966).

*Terrestrial plants:* As a group, terrestrial plants are fairly insensitive to ferrocyanide and free cyanides. As much as 10 g ferrocyanide/kg soil mix is needed to observe growth inhibition. Like microorganisms, some plants possess alternate respiration pathways and/or the ability to metabolize HCN. However, some plants do exhibit adverse effects. A 25% inhibition of seedling emergence was observed in radish plants at concentrations as low as **1.2 mg/kg**

(Environment Canada, 1995a). This represents the lowest concentration at which adverse effects to terrestrial plants have been reported.

*Terrestrial invertebrates:* While some invertebrates are resistant to cyanide or produce cyanides as a defensive mechanism, most demonstrate some level of sensitivity. The lowest free cyanide concentration inducing an adverse effect in terrestrial invertebrates is **4 mg/kg**, which caused mortality in 25% of earthworms (*Eisenia fetida*) exposed for 14 days (Environment Canada, 1995b).

*Terrestrial vertebrates:* Ferrocyanides have been approved as food additives and used as therapeutics. Rats exposed to 3200 mg/kg(bw)/day were unaffected (Dvorak *et al.*, 1971). For HCN, existing standards with a 7 to 8 fold safety margin, limit exposure to 5 $mg/m^3$ (Klaassen, 1966). The US EPA developed a subchronic reference dose (RfD) of 0.08 mg/kg(bw)/day for free cyanide ($CN^-$) from available research. From the available literature, the mammal most sensitive to adverse effects is the rabbit (*Oryctolagus* spp.). Ballantyne (1987) observed an $LD_{50}$ value of **0.6 mg/kg** bw. Among birds, mallard ducks (*Anas platyrhynchos*) appear the most sensitive exhibiting an $LD_{50}$ for oral ingestion of sodium cyanide of **2.7 mg/kg** (Henny *et al.*, 1994).

### *3.7.4 Risk characterization*

As previously stated, the greatest environmental danger from the use of sodium ferrocyanide is the ability of the ferrocyanide anion in solution to undergo photodecomposition resulting in the release of $CN^-$ and its subsequent hydrolysis to HCN. The process has been extensively examined by Broderius and Smith (1980) who reported the rate of reaction to be generally a direct function of light intensity (which depends on time of year, time of day, sky conditions), temperature and concentration, and an inverse function of pH and latitude. A maximum of five out of six of the available molecular cyanide can be released.

For assessment under Tier I and II assumptions, **Quotient** values were calculated for biota by dividing the highest measured and/or estimated free cyanide concentrations in water, air or soil by the individual **ENEVs**. The **ENEVs** used correspond to the **CTVs**, which are the lowest effect concentrations found in toxicity studies from the available literature divided by appropriate **application factors**.

#### 3.7.4.1 Tier I risk characterization

The Tier I assessment applied worst case condition correction factors in conjunction with typical Canadian location values to compute the photolysis rate. The reaction is proposed to occur at latitude 45° north at noon on a cloudless day of 4 °C. The rate under these conditions is 28.5%/hr. The cyanide so produced is considered to be conserved entirely within the considered environmental compartment.

*Cyanide concentration in water:* Calculating from the range of annual mean peak cyanide concentrations expected in runoff water which was determined earlier, it can be seen that the range of stoichiometric cyanide content is 0.087 to 870 ug $CN^-$/L. Given a 1-hour reaction window, the $CN^-$ released to water through photolysis gives a concentration ranging from 0.025 to 250 μg $CN^-$/L.

*Cyanide concentration in soil: Case I:* Using the maximal annual salt application rate (i.e.,10150 g/$m^2$), Tier I and soil Case I assumptions the stoichiometric content of $CN^-$ would be 1.35 mg $CN^-$/kg soil. After a 1-hour reaction window, the $CN^-$ released through photolysis would give a concentration of 0.39 mg $CN^-$/kg.

*Cyanide concentration in soil: Case II:* Using the maximal annual salt application rate (i.e.,10 150 g/$m^2$), Tier I and soil Case II assumptions the stoichiometric content of $CN^-$ would be 0.027 mg $CN^-$/kg soil. After a 1-hour reaction window, the $CN^-$ released through photolysis would give a concentration of 0.0078 mg $CN^-$/kg.

*Cyanide concentrations in air:* The volatilization rate of cyanide at concentrations of 0.1 to 0.5 mg/L is 0.22 mg $CN^-$/$m^2$/hour (Higgs, 1992). For Tier I purposes, a closed box model corresponding to a 10-cm layer of air above the roadway was used. After 1 hour, the maximum cyanide concentration in this layer would be 2.2 mg $CN^-$/$m^3$.

Quotient calculations were based on the highest estimated and measured free cyanide concentrations in water (i.e., 250 and 270 μg/L ) (Novotny *et al.* (1997) and were calculated as follows: **Quotient = EEV/ENEV.** Quotients above 1 suggest the need for a Tier II assessment.

For terrestrial organisms, quotient calculations were undertaken using the highest estimated free cyanide concentration in soil under Tier I assumptions (i.e., 0.39 mg/kg soil). No measured free cyanide soil concentrations were available in the literature. For birds and mammals, **EEVs** were calculated using a multipath model incorporating intake from soil, air and water.

### 3.7.4.2 Tier I conclusions

With the exception of terrestrial vertebrates and invertebrates, all quotients exceed 1 (Tables 24 and 25). Aquatic organisms appear particularly susceptible. A Tier II assessment is warranted.

### 3.7.4.3 Tier II risk characterization

The Tier II assessment endeavours to minimize any Tier I overestimates. Typical and measured variables are generally employed.

Rate of addition of sodium ferrocyanide has decreased over the past years. The 1997 addition rate of 80 mg $NaFe(CN)_6^-$/kg salt corresponding to 55.8 mg $Fe(CN)_6^-$/kg and 41.1 mg $CN^-$/kg road salt is more typical of present day use and will be used in Tier II.

Labadia and Buttle (1996) measured the pattern of road salt dispersal along a section of southern Ontario highway. Their observations show that slightly more than 50% of applications are redistributed to adjacent snowpack within a 3.7-m splash zone. This will also be taken into consideration in Tier II.

The ferrocyanide photolysis rate calculation was corrected to reflect an average daily light intensity and a condition of 70% clear sky effect. Corrections were also made to account for changes in initial ferrocyanide concentration. Overall Tier II assumptions produced an adjusted photolysis rate of 13.8% per hour.

*Cyanide concentration in water:* Based on Tier II assumptions, and the annual mean peak $Cl^-$ concentrations compiled by Morin and Perchanok (1998), the $CN^-$ concentration range in water after 1 hour was calculated to be 0.0039 to 39 µg/L.

*Cyanide concentration in soil – Case I:* Using the maximal annual salt application rate (i.e.,10 150 g/m$^2$), Tier II and soil Case I assumptions the soil concentration following the photolytic release of $CN^-$ from the available ferrocyanide would be 0.12 mg $CN^-$/kg soil after 1 hour.

*Cyanide concentration in soil – Case II:* Using the maximal annual salt application rate (i.e.,10 150 g/m$^2$), Tier II and soil Case II assumptions the soil concentration following the photolytic release of $CN^-$ from the available ferrocyanide would be 0.0024 mg $CN^-$/kg soil after 1 hour.

*Cyanide concentrations in air:* The volatilization rate of cyanide at concentrations of 0.1 to 0.5 mg/L is 0.22 mg $CN^-$/m$^2$/hour (Higgs, 1992). For this assessment it is assumed the available cyanide is completely transferred to the air above the roadway without dispersal and that the gaseous diffusion rate is the same as the interfacial diffusion rate. Under these conditions after 1 hour the maximum cyanide concentration in this layer would be 0.22 mg $CN^-$/m$^3$.

Quotient calculations were undertaken using the highest estimated free cyanide concentration in runoff water under Tier II assumptions (i.e., 39 µg/L) and the highest measured concentration of 41 µg/L derived as the geometric mean of measured values reported in the literature. The **CTVs** used in the Tier I assessment are used again in Tier II, but some application factors were modified to reflect a more realistic analysis. Quotients were calculated as follows: **Quotient = EEV/ENEV.**

Assessment of terrestrial organisms was conducted using the highest estimated free cyanide concentration in soil under Tier II assumptions (i.e., 0.12 mg/kg soil). No measured free

cyanide soil concentrations were available in the literature. Calculation of **EEVs** for birds and mammals was the same as in Tier I.

3.7.4.4 Tier II conclusions

Based on the calculated quotients (Tables 26 and 27), a Tier III assessment should be conducted for aquatic organisms.

3.7.4.5 Tier III risk characterization

Tier I and Tier II analysis have shown sodium ferrocyanide to have the potential to negatively impact the aquatic environment. Tier III assessment quantifies the probability of adverse effect within the aquatic compartment.

As already stated, photolytic release of $CN^-$ from $Fe(CN)_6^{-4}$ remains the most serious concern from ferrocyanide releases to the environment. Total photolysis across the relevant wavelengths and losses due to volatilization can be mathematically modelled, and from these models, the concentration of $CN^-$ in solution can be calculated for any given time after the salt application event. These calculations were part of the Tier III assessment

*Assumptions*

For purposes of Tier III, the following assumptions and correction factors were used in estimating ferrocyanide photolysis and volatilization rates. Because photolysis is a function of water depth and clarity, ferrocyanide was considered to be contained within the first 20 cm and clarity measurements from a range of water bodies were used. Likewise, the reaction rate is a function of date, time of day, sky conditions and temperature. Calculations were therefore made for every hour of the day for January 1, April 1, June 21 and September 21 under conditions of 70% clear sky effect with Henry's law constant corrected for an average temperature of 4° C. The June and September calculations are for comparison purposes only as salting does not occur in these months. The observations of Labadia and Buttle (1996), who reported that approximately 50% of an initial salt application is redistributed to the adjacent snow pack were, as previously, taken into consideration. Both stream and wind velocities were estimated from direct Canadian source measurements. Mean stream current was set at 0.52 m $sec^{-1}$ and wind velocity was set to 64.5, 60.9, 49.6 and 48.9 m $sec^{-1}$ m for the months of January, April, June and September, respectively. The Cl runoff water concentrations were selected from the range of values collected by Morin and Perchanok (2000). The probability of selection of a given concentration for inclusion in a calculation was a function of the size of the area reporting that concentration. Sodium ferrocyanide addition rates were selected for inclusion in calculations on a probability basis reflecting the percentage of the market served by the corresponding source mine.

*Estimation of the frequency of occurrence of toxic events*

Calculations were conducted by randomly selecting each variable from the appropriate frequency distribution. Variables included chloride concentration in runoff water, concentration of ferrocyanide in salt, current speed, wind speed and attenuation coefficient. Photodecomposition–volatilization curves were generated for each date. The maximal free cyanide value so produced was then recorded. This procedure was repeated 10 000 times and the resulting "Maximum Free Cyanide Observed" values ($EEV_{Max}$) were sorted into ascending order. The CTVs for each aquatic organism were then compared to these randomly generated distributions and the probability that an exposure event would equal or exceed the CTV was determined. The procedure was run in duplicate using data derived from across Canada and from the most heavy use region, the Quebec City to Windsor corridor.

As extensive data on salt use by many Canadian municipalities were available, the above procedure was repeated using the salting data from three municipalities selected as representative of the highest, average and lowest Canadian municipal use. The selected municipalities were: La Tuque, Quebec; Newmarket, Ontario; and White River, Ontario. Results are briefly summarized below. Full results are presented in the supporting document entitled *Effects of Sodium Ferrocyanide Derived for Road Salting on the Ecosystem* (Letts, 2000).

*Tier III results and conclusions*

*Aquatic microorganisms:* Following analysis, it appears that *Pseudomonas putida* would be adversely affected in 100% of theoretical exposures. However, other aquatic microorganisms for which data were available are not as sensitive to cyanide. In the highest use municipality, *Microregma heterostoma* would be expected to be affected adversely in as many as 60% of cases. However, the use in that municipality is twice or greater than the level in all but the two next highest users in 90 Canadian cities. No adverse effects are indicated for any of the other five aquatic microorganisms considered. Ferrocyanide from road salts may be viewed as not posing a significant threat to this category of biota in most instances.

*Aquatic plants:* Results demonstrate only *Scenedesmus quadricauda* to be adversely affected in 16 to 28% of possible exposures, with a value as high as 82% in the municipality with highest use. Values therefore indicate low level of risk for most aquatic plants at most sites and times, although there is a potential for moderate effects at certain times for certain sensitive species.

*Aquatic invertebrates:* Adverse effects to *C. asperrimus* may occur on as many as 34% of exposures during April in the Quebec to Windsor corridor. The likelihood of negative consequence falls to less than 25% of cases for any other location or date. As expected, risk is greater in the municipality with highest use. No other organism is shown to risk harm at greater

than 3.5% of exposure levels. Negative effects within this group are restricted in time and location. Generally, members of this group are not considered at serious risk but significant exposure of sensitive species may occur.

*Aquatic vertebrates:* The highest potential for significant exposures was indicated for aquatic vertebrates. Toxicological data for *Lepomis macrochirus*, *Oncorhynchus mykiss* and *P. promelas* were derived for conditions of 57, 20 and 256 days' exposure. Toxicological results for *Oncorhynchus kisutch* are from a study that reported swimming impairment after a 2-hour exposure to 10 µg/L of free cyanide. Other studies report Rainbow trout 96-hr $LC_{50}$ to be 17 µg/L (Higgs, 1992), 27µg/L (Smith *et al.*, 1979) and 28 µg/L (Kovacs, 1979; Kovacs and Leduc, 1982). The probability of occurrence of concentrations equal or greater to these are respectively 52.6%, 26.8% and 25.2% for January, and 67.2%, 36.2% and 33.8% for April for locations within the Quebec–Windsor corridor. This is the area of higher concentrations of the two broad-based sources of data.

In the environment, free cyanide would dissipate quickly relative to the duration of the experimental toxicity exposure times. In evaluating risk, the location of possible exposure must also be taken into account. The exposure levels estimated here would be expected only to exist in roadside ditches or streams. Thus, aquatic vertebrates could be exposed to risks as a consequence of sodium ferrocyanide use. However, significant risks are expected to be localized in time and place and exposure may be transitory.

### *3.7.5 Proposed conclusion for ferrocyanides*

The Tier I and II assessments indicate that at present levels of road salt use, potential adverse effects are limited to aquatic biota. Assessment at the Tier III level indicates limited potential for sodium ferrocyanide use to cause negative consequences to aquatic microorganisms, aquatic plants and aquatic invertebrates. However, Tier III assessment points to possible adverse exposure events for the more sensitive aquatic vertebrates. The possible threat is attenuated by the limitations of duration and location of exposure.

## 3.8 Proposed conclusions

CEPA 1999 64(a) and 64(b): Based on available data, it is proposed that the substance road salts is entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity, and that constitute or may constitute a danger to the environment on which life depends. Therefore, it is proposed that road salts be considered "toxic" under Paragraphs 64(a) and 64(b) of the *Canadian Environmental Protection Act, 1999* (CEPA 1999).

Proposed overall conclusion: Based on critical assessment of relevant information, it is proposed that the substance road salts be considered to be "toxic" as defined in Section 64 of CEPA 1999.

### 3.9 Considerations for follow-up (further action)

The use of de-icing agents is an important component of strategies to keep roadways open and safe during the winter and minimize traffic crashes, injuries and mortality under icy and snowy conditions. These benefits were recognized by the Expert Advisory Panel on the second Priority Substances List (PSL), even as they recommended that this assessment of potential impacts on environmental organisms be conducted. Any measures developed as a result of this assessment must never compromise human safety; selection of options must be based on optimization of winter road maintenance practices so as to not jeopardize road safety, while minimizing the potential for harm to environmental organisms. Any action taken to reduce impacts on environmental organisms is likely also to reduce potential for contamination of groundwater-based drinking water supplies, which is clearly desirable.

Management should focus on key sources in areas where the assessment has indicated concerns. These relate to:

Patrol yards: Key concerns relate to contamination of groundwater at patrol yards, which in turn can be associated with problems of groundwater quality, discharge to surface water and effects on aquatic biota; in addition, runoff can result in direct impacts on surface water and on vegetation. Based on surveys and reviews, salt losses from patrol yards are associated with loss at storage piles — including salt piles as well as piles of sand and gravel to which salts have been added — and during the handling of salts, relating to both storage and loading of trucks. Measures should therefore be considered to ensure storage of salt and abrasives to reduce losses through weathering, during transfers, and management of stormwater and equipment washwater.

Roadway application: Key environmental concerns have been associated with areas of high salt use and high road density. Regions of southern Ontario and Quebec and the Maritimes have been shown to have the highest rate of salt use on an area basis and as such have the highest potential for contamination of soils and surface and groundwater by chloride ions as a result of roadway applications. In addition, urban areas in other parts of the country where high amounts of salts are applied are of potential concern. In rural areas, surface waters receiving drainage from roadways may also be susceptible to contamination. Therefore, measures should be considered to reduce the overall chloride use while ensuring maintenance of roadway safety.

Snow disposal: Key environmental concerns relate to eventual loss of meltwater into surface water and into soil and groundwater at snow disposal sites. Measures should be considered to minimize percolation into soil and groundwater and direct release into water; in

cases of release into surface water via storm sewer systems, measures ensuring sufficient dilution before release should also be considered.

Ferrocyanides: Assessment indicates possible adverse exposure for the more sensitive aquatic vertebrates in areas of very high use of road salts. Risks could be reduced by reducing total salt use or reducing content of ferrocyanides in road salt formulations. To reduce the possibility of exposure, producers of road salts could consider reducing the addition rate of rerrocyanide to road salt. Any reduction in total salt use would be expected to result in an equivalent reduction in release of ferrocyanides.

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## APPENDIX A: Search Strategies Employed for Identification of Relevant Data

### Environmental assessment

Data relevant to the assessment of whether the substance road salts is "toxic" to the environment under CEPA 1999were identified from existing review documents, published reference texts and on-line searches conducted between January and May 1996 of the following databases:

Aqualine (1990–1996), ASFA (Aquatic Sciences and Fisheries Abstracts, Cambridge Scientific Abstracts; 1996), BIOSIS (Biosciences Information Services; 1990–1996), CAB (Commonwealth Agriculture Bureaux; 1990–1996), CESARS (Chemical Evaluation Search and Retrieval System, Ontario Ministry of the Environment and Michigan Department of Natural Resources; 1996), Chemical Abstracts (Chemical Abstracts Service, Columbus, Ohio; 1990–1996), CHRIS (Chemical Hazard Release Information System; 1964–1985), Current Contents (Institute for Scientific Information; 1990–1992, 1996), ELIAS (Environmental Library Integrated Automated System, Environment Canada library; January 1996), Enviroline (R.R. Bowker Publishing Co.; November 1995 – June 1996), Environmental Abstracts (1975 – February 1996), Environmental Bibliography (Environmental Studies Institute, International Academy at Santa Barbara; 1990–1996), GEOREF (Geo Reference Information System, American Geological Institute; 1990–1996), HSDB (Hazardous Substances Data Bank, U.S. National Library of Medicine; 1990–1996), Life Sciences (Cambridge Scientific Abstracts; 1990–1996), NTIS (National Technical Information Service, U.S. Department of Commerce; 1990–1996), Pollution Abstracts (Cambridge Scientific Abstracts, U.S. National Library of Medicine; 1990–1996), POLTOX (Cambridge Scientific Abstracts, U.S. National Library of Medicine; 1990–1995), RTECS (Registry of Toxic Effects of Chemical Substances, U.S. National Institute for Occupational Safety and Health; 1996), Toxline (U.S. National Library of Medicine; 1990–1996), TRI93 (Toxic Chemical Release Inventory, U.S. Environmental Protection Agency, Office of Toxic Substances; 1993), US EPA-ASTER (Assessment Tools for the Evaluation of Risk, U.S. Environmental Protection Agency; up to December 21, 1994), WASTEINFO (Waste Management Information Bureau of the American Energy Agency; 1973 – September 1995) and Water Resources Abstracts (U.S. Geological Survey, U.S. Department of the Interior; 1990–1996). Reveal Alert was used to maintain an ongoing record of the current scientific literature pertaining to the potential environmental effects of road salts.

In addition, the Transportation Association of Canada has reviewed information on sodium calcium road salt as part of its Road Salt Management Initiative (TAC, 1999).

Data searches were done by individual working groups preparing separate components of the supporting documentation. Search strategies or data sources are provided in individual reports.

Data obtained after May 2000 were not considered in this assessment.

**Table 1: Road salts and related roadway maintenance chemicals**

| Substance | Specific application | Application rate (kg/2-lane km) |
|---|---|---|
| sodium chloride, NaCl | road de-icing and anti-icing, de-icing additive for sand | 130 (typical) 25–350 (range) |
| calcium chloride, $CaCl_2$ | dust suppressant, road construction | 2.4–5.4 |
| | road anti-icing, prewetting, de-icing additive for sand | not applied straight |
| | road anti-icer | 50–70 kg/t asphalt (as Verglimit) |
| mixture of sodium/calcium chloride | road de-icer | 130 |
| magnesium chloride, $MgCl_2$ | road de-icer, de-icing additive | 595 L/2-lane km (as Freezegard) |
| | off-road dust suppressant | No data |
| mixture of sodium/ magnesium chloride | road de-icer | 130 (as Qwiksalt) |
| potassium chloride, KCl | road de-icer (contained in potash mine tailings) | No data |
| oil field brine | dust suppressant | No data |
| sodium/ferric ferrocyanide | anti-caking additive for NaCl | 0.3 – 0.13 (estimate includes both substances) |
| calcium magnesium acetate, CMA [$CaMg(C_2H_3O_2)_2$] | alternative road de-icer, anti-icer, potential airport runway de-icer | 220 |
| sodium formate, $NaCH_2O_2$ | potential road de-icer | 130 |
| urea, $CO(NH_2)_2$ | airport runway de-icer, anti-icer | 210 |
| sodium acetate, $NaC_2H_3O_2$ | potential airport runway de-icer | No data |
| potassium acetate, $KC_2H_3O_2$ | alternative airport runway de-icer, anti-icer | No data |
| ethylene glycol, $C_2H_6O_2$ | airplane de-icer | No data |
| sand, $SiO_2$ | abrasive | 570 |
| cinders | abrasive | No data |

**Table 2: Physical-chemical properties of road salts***

| Substance | CAS # | Specific application | Form | Molec. weight | Density | Melting point °C | Boiling point °C | Eutectic** temp. °C | Working** * temp.°C | Water solubility g/100 mL (°C) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| sodium chloride, NaCl | 7647-14-5 | road de-icer, de-icing additive | solid | 58.44 | 2.165 | 801 | 1413 | -21 | -9 to -28 | 35.7 (0) | 39.12 (100) |
| calcium chloride, $CaCl_2$ | 10043-52-4 | road de-icer, de-icing additive | flake | 110.99 | 2.15 | 772 | 1935 | -51.1 | < -23 | 37.1 (0) | 42.5 (20) |
| $CaCl_2 \cdot 2H_2O$ (37%) | 10035-04-8 | anti-icer, prewetter | liquid | 147.02 | 1.85 | deh. 176 | deh. 176 | | < -18 | 97.7 | 326 |
| 35% $CaCl_2$ | | dust suppressant | brine | | 1.35 | -7 | 116 | | | very soluble | very soluble |
| mixture of sodium/calcium chloride (80/20 mix) | | road de-icer | solid | | | | | n.a. | -12 | | |
| | | road anti-icer | liquid | | | | | n.a. | -12 | | |
| magnesium chloride, $MgCl_2$ | 7786-30-3 | road de-icer, de-icing additive | solid | 95.21 | 2.316-2.33 | 714 | 1412 | -33.3 | -15 | 54.25 (20) | 72.7 (100) |
| | | road anti-icer dust suppressant | liquid brine | | | | | -33.3 | -15 | | |
| mixture of sodium/magnesium chloride (80/20 mix) | | road de-icer | solid | | | | | | < -15 | | |
| potassium chloride, KCl | 7447-40-7 | alternative road de-icer | solid | 74.55 | 1.984 | 770 | sub.1500 | -10.5 | -3.89 | 34.4 | 56.7 (100) |
| sodium ferrocyanide, $Na_4Fe(CN)_6 \cdot 10H_2O$ | 13601-19-9 | anti-caking additive | | 484.07 | 1.458 | | | | | 31.85 (20) | 156.5 (98) |
| ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$ | 14038-43-8 | anti-caking additive | solid | 859.25 | | dec. | | | | insoluble | insoluble |

* Physical-chemical properties are from Weast *et al.* (1989) and Chang *et al.* (1994).

** Eutectic temperature refers to the lowest temperature at which the substance will melt ice.

*** Working temperature refers to the lowest effective de-icing temperature.

**Table 3: Total sodium chloride road salt loadings in Canada, Winter 1997–98***

| Province | Provincial (used)* | Estimated county + municipal* | Total provincial/ county/ municipal | Estimated commercial & industrial ** | Grand total NaCl road salt loading in Canada (tonnes) |
|---|---|---|---|---|---|
| British Columbia | 83 458 | 48 199 | 131 657 | 9874 | **141 531** |
| Alberta | 101 063 | 67 870 | 168 933 | 12 670 | **181 603** |
| Saskatchewan | 44 001 | 4844 | 48 845 | 3663 | **52 508** |
| Manitoba | 36 780 | 28 256 | 65 036 | 4878 | **69 914** |
| Ontario | 592 932 | 1 123 653 | 1 716 585 | 128 744 | **1 845 329** |
| Quebec | 609 550 | 827 205 | 1 436 755 | 107 757 | **1 544 512** |
| New Brunswick | 189 093 | 75 826 | 264 919 | 19 869 | **284 788** |
| Prince Edward Island | 23 051 | 4300 | 27 351 | 2051 | **29 402** |
| Nova Scotia | 270 105 | 77 761 | 347 866 | 26 090 | **373 956** |
| Newfoundland | 159 200 | 47 558 | 206 758 | 15 507 | **222 265** |
| Yukon | 1 791 | 120 | 1911 | 143 | **2054** |
| Northwest Territories*** | 1 846 | 0 | 1846 | 138 | **1984** |
| **Total** | **2 112 870** | **2 305 592** | **4 418 462** | **331 385** | **4 749 847** |

* From Morin and Perchanok, 2000.

** Commercial and industrial road salt use is assumed to be at 7.5% of provincial and municipal use (7.5% based on estimate by Cheminfo, 1999).

*** Including Nunavut.

**Table 4: Estimated quantity of calcium chloride used on roadways in Canada in a typical year**

| Province | Tonnes $CaCl_2$ |
|---|---|
| British Columbia | 12 573 |
| Alberta | 6985 |
| Saskatchewan | 2794 |
| Manitoba | 6985 |
| Ontario | 45 405 |
| Quebec | 20 956 |
| New Brunswick | 1746 |
| Prince Edward Island | 349 |
| Nova Scotia | 5169 |
| Newfoundland | 839 |
| Yukon | 1397 |
| Northwest Territories | 2794 |
| **Canada** | **107 992** |

**Table 5: Total chloride loadings**

| Province | Tonnes chloride |
|---|---|
| British Columbia | 93 900 |
| Alberta | 114 641 |
| Saskatchewan | 33 642 |
| Manitoba | 46 880 |
| Ontario | 1 148 570 |
| Quebec | 950 444 |
| New Brunswick | 173 896 |
| Prince Edward Island | 18 061 |
| Nova Scotia | 230 182 |
| Newfoundland | 135 384 |
| Yukon Territory | 2139 |
| Northwest Territories | 2989 |
| **Total chloride** | **2 950 728** |

**Table 6: Total volume of waste snow and quantity of salt used in certain Canadian cities during winter 1997–98**

| City | Total snow volume (m3) * | Quantity of salt used (tonnes) |
|---|---|---|
| Vancouver | Less than 100 000 | 2254 |
| Calgary | 320 000 | 20 428 |
| Regina | 150 000 | 2067 |
| Winnipeg | 175 000 | 24 525 ** |
| Toronto (before amalgamation) | 1 500 000 | 17 884 |
| Ottawa-Carleton | 1 220 000 | 68 000 |
| Montréal | 11 258 000 | 60 000 *** |
| Quebec City | 3 000 000 | 35 000 |
| Moncton | 159 000 | 12 695 |
| Halifax | N/A | 41 679 |
| Charlottetown | N/A | 2300 |
| St. John's | N/A | 21 530 |

* These quantities are approximate and vary yearly with snowfall amount.

** Plus 100 000 tonnes of a sand-salt mix containing 5% NaCl.

*** Plus 39 000 tonnes of a sand-gravel mix (1:9 for sidewalks and 5:5 for streets) during freezing rain.

**Table 7: Snow disposal methods used in certain Canadian cities, winter 1997–98**

| City | Waste snow disposal (% of total snow volume) | | | | |
|---|---|---|---|---|---|
| | Surface dumps | Quarries | Sewer chutes | Melters | Waterways or sea |
| Vancouver | 10 | - | - | - | 90 |
| Calgary | 100 | - | - | - | - |
| Regina | 100 | - | - | - | - |
| Winnipeg | 100 | - | - | - | - |
| Toronto | 90 | - | - | 10 | - |
| Ottawa-Carleton | 100 | - | - | - | - |
| Montréal | 25 | 37.7 | 18 | - | 19.3 |
| Quebec City | 100 | - | - | - | - |
| Moncton | 100 | - | - | - | - |
| Halifax | - | - | - | - | 100 |
| St. John's | - | - | - | - | 100 |

From Delisle and Dériger, 2000.

**Table 8: Number of provincial patrol yards and NaCl and abrasive use by province**

| Province | # of patrol yards | Total NaCl used | Total abrasives used | Tonnes of NaCl/ patrol yard | Tonnes of abrasives/ patrol yard |
|---|---|---|---|---|---|
| BC | 166 | 78 538 | 720 717 | 473 | 4342 |
| Alta | 71 | 121 035 | 300 464 | 1705 | 4232 |
| Sask | 86 | 44 001 | 30 939 | 512 | 360 |
| Man | 67 | 36 780 | 37 800 | 549 | 564 |
| Ont | 158 | 592 932 | 555 859 | 3753 | 3518 |
| Que | 478 | 609 550 | 548 996 | 1275 | 1149 |
| NB | 95 | 189 093 | 376 705 | 1990 | 3965 |
| PEI | 10 | 23 051 | 85 735 | 2305 | 8574 |
| NS | 82 | 270 105 | 81 943 | 3294 | 999 |
| Nfld | 44 | 159 200 | 269 460 | 3618 | 6124 |
| Yukon | 23 | 1 791 | 38 000 | 78 | 1652 |
| NWT | 10 | 1 846 | 11 400 | 185 | 1140 |
| **Total** | **1290** | **2 127 922** | **3 058 017** | | |

**Table 9: Estimate of magnitude of salt loss at patrol yards**

| Patrol yard type | Loss from management area of 190 yards | Percentage of road total salt use (590 000 tonnes) |
|---|---|---|
| **Option 1** – Best management practices patrol yards – indoor storage for mixed abrasive and salt piles | 1290 tonne salt/year | 0.2% |
| **Option 2**- Patrol yards where salt piles are stored indoors and abrasive piles are stored outdoors. | 9900 tonne salt/year | 1.7% |
| **Option 3** – Patrol yards where neither abrasive nor salt piles are stored indoors | 128 000 tonne salt/year | 22% |

**Table 10: Chloride concentrations (mg/L) in various streams in the Toronto Remedial Cation Plan Watershed for 1990–96**

| Station location | # of obs. | Min. | Max. | Mean | Median | % Frequency exceedence | |
|---|---|---|---|---|---|---|---|
| | | | | | | 250 mg/L | 500 mg/L |
| Etobicoke Creek | | | | | | | |
| at Derry Road | 38 | 10 | 3780 | 278 | 135 | 18 | 8 |
| at Burnhamthorpe Road | 40 | 0 | 2670 | 392 | 206 | 40 | 20 |
| at Highway #2 | 74 | 43 | 2140 | 351 | 208 | 38 | 19 |
| Mimico Creek | | | | | | | |
| at Highway #2 | 37 | 51 | 3470 | 553 | 276 | 62 | 22 |
| Black Creek | | | | | | | |
| at Scarlett Road | 38 | 20 | 4310 | 495 | 248 | 47 | 21 |
| Highland Creek | | | | | | | |
| at Highway Creek Park | 55 | 22 | 1390 | 310 | 220 | 42 | 13 |

Source: Provincial Water Quality Monitoring Network.

**Table 11: Summary of Tier 2 calculations. CTV is the Critical Toxicity Value, EEV is the estimated exposure value (1 000 mg/L of chloride) and ENEV is the Estimated No Effects Value (CTV/application factor). (See text for further explanation.)**

| Organism | Exposure time/endpoint | CTV Cl (mg/L) | Reference | Application factor | EEV/ENEV |
|---|---|---|---|---|---|
| 1. Bacteria<br>*E. coli* | 2-hr, 50% degradation of RNA | 5321 | Ito *et al.*,1977 | 100 | 18.8 |
| 2. Fungi<br>Unknown aquatic fungi | 48-hr, increased sporulation | 400 | Sridhar and Barlocher, 1997 | 100 | 250 |
| 3. Protozoans<br>*Euglena gracilis* | 7-d, 16% reduction of cells cultured in light | 3548 | Gonzalez-Moreno *et al.*, 1997 | 10 | 2.8 |
| 4. Phytoplankton<br>*Nitzschia linearis* | 120-hr, 50% reduction in number of cells | 1475 | Patrick *et al.*, 1968 | 100 | 67.8 |
| 5. Macrophytes<br>*Sphagnum fimbriatum* | 45-d, 43% reduction in growth | 1500 | Wilcox, 1984 | 100 | 66.7 |
| 6. Zooplankton<br>*Ceriodaphnia dubia* | 7-d, 50% mortality | 1470 | Birge *et al.*, 1985; Cowgill and Milazzo, 1990 | 100 | 68.0 |
| 7. Benthic invertebrates<br>*Nais variabilis* | 48-hr $LC_{25}$ | 1214 | Hamilton *et al.*, 1975 | 10 | 8.2 |
| 8. Amphibians<br>*Xenopus laevis* | 7-d $EC_{50}$ | 1524 | Beak, 1999 | 100 | 65.6 |
| 9. Fish<br>*Oncorhynchus mykiss* | 7-d $EC_{25}$, egg/embryo | 989 | Beak, 1999 | 10 | 10.1 |

**Table 12: Toxicity responses of organisms to sodium chloride for exposures less than one day**

| Species | Taxon | NaCl (mg/L) | Cl (mg/L) | Response | Time (hr) | Reference |
|---|---|---|---|---|---|---|
| *Salvelinus fontinalis* | Brook trout | 50 000 | 30 330 | $LC_{50}$ | 0.25 | Phillips, 1944 |
| *Lepomis macrochirus* | Bluegill | 20 000 | 12 132 | $LC_{47}$ | 6 | Waller *et al.*, 1996 |
| *Oncorhynchus mykiss* | Rainbow trout | 20 000 | 12 132 | $LC_{40}$ | 6 | Waller *et al.*, 1996 |
| *Chironomus attenatus* | Chironomid | 9995 | 6063 | $LC_{50}$ | 12 | Thorton and Sauer, 1972 |
| *Escherichia coli* | Bacteria | 8767 | 5318 | $EC_{50}$ | 2 | Ito *et al.*, 1977 |

**Table 13: Toxicity responses of organisms to sodium chloride for exposures of one day**

| Species | Taxon | NaCl (mg/L) | Cl (mg/L) | Response | Reference |
|---|---|---|---|---|---|
| *Lepomis macrochirus* | Bluegill | 14 100 | 8553 | $LC_{50}$ | Doudoroff and Katz, 1953 |
| *Daphnia magna* | Cladoceran | 7754 | 4704 | $LC_{50}$ | Cowgill *et al.*, 1990 |
| *Cirrhinius mrigalo* | Indian carp fry | 7500 | 4550 | $LC_{50}$ | Gosh and Pal,1969 |
| *Labeo rohoto* | Indian carp fry | 7500 | 4550 | $LC_{50}$ | Gosh and Pal,1969 |
| *Catla catla* | Indian carp fry | 7500 | 4550 | $LC_{50}$ | Gosh and Pal, 1969 |
| *Daphnia pulex* | Cladoceran | 2724 | 1652 | $LC_{50}$ | Cowgill *et al.*, 1990 |
| *Ceriodaphnia dubia* | Cladoceran | 2724 | 1 652 | $LC_{50}$ | Cowgill *et al.*, 1990 |

**Table 14: Four-day $LC^{50}$ of various taxa exposed to sodium chloride**

| Species | Taxon | NaCl (mg/L) | Cl (mg/L) | Sources |
|---|---|---|---|---|
| *Ceriodaphnia dubia* | Cladoceran | 2308 | 1400 | Cowgill *et al.*, 1990 |
| *Daphnia pulex* | Cladoceran | 2422 | 1470 | Birge *et al.*, 1985 |
| *Ceriodaphnia dubia* | cladoceran | 2630 | 1596 | WI SLOH, 1985 |
| *Daphnia magna* | cladoceran | 3054 | 1853 | Anderson, 1948 |
| *Daphnia magna* | cladoceran | 3939 | 2390 | Arambasic *et al.*, 1995 |
| *Physa gyrina* | snail | 4088 | 2480 | Birge *et al.*, 1985 |
| *Lirceus fontinalis* | isopod | 4896 | 2970 | Birge *et al.*, 1985 |
| *Catla catla* | Indian carp fry | 4980 | 3021 | Gosh and Pal, 1969 |
| *Labeo rohoto* | Indian carp fry | 4980 | 3021 | Gosh and Pal, 1969 |
| *Cirrhinius mrigalo* | Indian carp fry | 4980 | 3021 | Gosh and Pal, 1969 |
| *Daphnia magna* | cladoceran | 6031 | 3658 | Cowgill *et al.*, 1990 |
| *Cricotopus trifascia* | chironomid | 5192 | 3795 | Hamilton *et al.*, 1975 |
| *Chironomus attenatus* | chironomid | 6637 | 4026 | Thorton and Sauer, 1972 |
| *Hydroptila angusta* | caddisfly | 5526 | 4039 | Hamilton *et al.*, 1975 |
| *Daphnia magna* | cladoceran | 6709 | 4071 | WI SLOH, 1985 |
| *Anaobolia nervosa* | caddisfly | 7014 | 4255 | Sutcliffe, 1961b |
| *Limnephilus stigma* | caddisfly | 7014 | 4255 | Sutcliffe, 1961b |
| *Carassius auratus* | goldfish | 7341 | 4453 | Adelman *et al.*, 1976 |
| *Pimephales promelas* | fathead minnow | 7650 | 4640 | Adelman *et al.*, 1976 |
| *Pimephales promelas* | fathead minnow | 7681 | 4600 | WI SLOH, 1985 |
| *Lepomis macrochirus* | bluegill | 9627 | 5840 | Birge *et al.*, 1985 |
| *Culex sp.* | mosquito | 10 254 | 6222 | Dowden and Bennett |
| *Pimephales promelas* | fathead minnow | 10 831 | 6570 | Birge *et al.*, 1985 |
| *Oncorhynchus mykiss* | rainbow trout | 11 112 | 6743 | Spehar,1987 |
| *Lepomis macrochirus* | bluegill | 12 964 | 7864 | Trama, 1954 |
| *Gambusia affinis* | mosquito fish | 17 500 | 10 616 | Wallen *et al.*, 1957 |
| *Anguilla rostrata* | American eel, glass eel stage | 17 969 | 10 900 | Hinton and Eversole, 1978 |
| *Anguilla rostrata* | American eel, black eel stage | 21 571 | 13 085 | Hinton and Eversole, 1979 |

**Table 15: Seven-day $LC^{50}$ and $EC^{50}$ of various taxa exposed to sodium chloride. $LC^{50}/EC^{50}$ ratio calculated for studies where both parameters were estimated (i.e., Cowgill and Milazzo, 1990 and Beak, 1999).**

| Species | Taxon | NaCl (mg/L) | Cl (mg/L) | Response | Sources |
|---|---|---|---|---|---|
| *Ceriodaphnia dubia* | cladoceran | 2077 | 1261 | $LC_{50}$ | Cowgill and Milazzo, 1990 |
| *Xenopus leavis* | frog embryo | 2940 | 1784 | $LC_{50}$ | Beak, 1999 |
| *Daphnia magna* | cladoceran | 6031 | 3660 | $LC_{50}$ | Cowgill and Milazzo, 1990 |
| *Pimephales promelas* | fathead minnow larvae, | 5490 | 3330 | $LC_{50}$ | Beak, 1999 |
| *Pimephales promela* | fathead minnow embryos, survival | 1440 | 874 | $LC_{50}$ | Beak, 1999 |
| *Ceriodaphnia dubia* | cladoceran, mean brood size | 1761 | 1068 | $EC_{50}$ | Cowgill and Milazzo, 1990 |
| *Ceriodaphnia dubia* | cladoceran, total progeny | 1761 | 1088 | $EC_{50}$ | Cowgill and Milazzo, 1990 |
| *Ceriodaphnia dubia* | cladoceran, mean number of broods | 1991 | 1208 | $EC_{50}$ | Cowgill and Milazzo, 1990 |
| *Oncorhynchus mykiss* | rainbow trout egg embryo, survival | 2400 | 1456 | $LC_{50}$ | Beak, 1999 |
| *Nitschia linearais* | diatom, cell numbers | 2430 | 1474 | $EC_{50}$ | Gonzalez-Moreno *et al.* 19xx 1997 |
| *Xenopus leavis* | frog embryo, survival | 2510 | 1523 | $LC_{50}$ | Beak, 1999 |
| *Oncorhynchus mykiss* | rainbow trout embryo/alvin, survival | 2630 | 1595 | $LC_{50}$ | Beak, 1999 |
| *Daphnia magna* | cladoceran, mean brood size | 4040 | 2451 | $EC_{50}$ | Cowgill and Milazzo, 1990 |
| *Daphnia magna* | cladoceran, total progeny size | 4282 | 2599 | $EC_{50}$ | Cowgill and Milazzo, 1990 |
| *Daphnia magna* | cladoceran, dry weight | 4310 | 2616 | $EC_{50}$ | Cowgill and Milazzo, 1990 |
| *Daphnia magna* | cladoceran, mean number of broods | 5777 | 3506 | $EC_{50}$ | Cowgill and Milazzo, 1990 |
| *Pimephales promelas* | fathead minnow larvae, growth | 4990 | 3029 | $EC_{50}$ | Beak, 1999 |

**Table 16: Predicted cumulative percentage of species affected by chronic exposures to chloride (mg/L). Also shown are the upper and the lower 95% confidence limit. Data are from Figure 22.**

| Cumulative % of species affected | Mean chloride concentration | Lower confidence interval | Upper confidence interval |
|---|---|---|---|
| 5 | 212.6 | 135.9 | 289.5 |
| 10 | 237.9 | 162.3 | 313.6 |
| 25 | 328.7 | 260.2 | 397.2 |
| 50 | 563.2 | 504.8 | 621.7 |
| 75 | 963.7 | 882.3 | 1 045.1 |
| 90 | 1 341.1 | 1 253.8 | 1 428.4 |

**Table 17: Sodium chloride tolerance of selected plant species in the salt-impacted mat zone of Pinhook Bog, Indiana**

| Scientific name | Common name | Tolerance (mg/L) | | |
|---|---|---|---|---|
| | | NaCl | Na | Cl |
| *Bidens connata* | Purple-stemmed tickseed | 1030 | 405 | 625 |
| *Pyrus floribunda* | Purple chokeberry | 1070 | 420 | 649 |
| *Hypericum virginicum* | Marsh St. John's wort | 1070 | 420 | 649 |
| *Sphagnum* | Bog moss | 770 | 303 | 467 |
| *Solidago graminifolia* | Grass-leafed goldenrod | 760 | 299 | 461 |
| *Vaccinium corymbosum* | Highbush blueberry | 580 | 228 | 352 |
| *Vaccinium atrococcum* | Black highbush blueberry | 400 | 157 | 243 |
| *Drosera intermedia* | Oblong leafed sundew | 360 | 142 | 218 |
| *Nemopanthus mucronata* | Mountain holly | 280 | 110 | 170 |
| *Larix laricina* | Tamarack | 280 | 110 | 170 |

Source: Wilcox, 1982.

**Table 18: pH, total phosphorus (TP) and chloride (Cl-) optima for selected diatom species in the northeastern United States**

| Species | pH | TP (µg/L) | Cl- (mg/L) |
|---|---|---|---|
| *Achnanthes altaica* | 6.8 | 7 | 0.7 |
| *Achnanthes clevei* | 8.1 | 7 | 8.7 |
| *Amphora ovalis* | 8.0 | 22 | 4.2 |
| *Amphora perpusilla* | 8.3 | 25 | 21.0 |
| *Cyclotella meneghiniana* | 8.3 | 66 | 39.5 |
| *Cymbella cesatii* | 7.8 | 10 | 0.7 |
| *Fragilaria crotonensis* | 8.0 | 14 | 6.9 |
| *Navicula bremensis* | 6.2 | 7 | 0.5 |
| *Nitzschia linearis* | 7.4 | 8 | 0.8 |
| *Stephanodiscus niagrae* | 8.1 | 16 | 10.5 |
| *Synedra ulna* | 7.9 | 15 | 4.5 |
| *Tabellaria fenestrata* | 7.5 | 13 | 1.8 |
| *Tabellaria quadriseptata* | 5.5 | 11 | 1.1 |

Source: Dixit *et al.*, 1999.

**Table 19: Range of threshold values estimated for soil and water for various forms of plants**

| Pathway | Form | Plant form | Threshold type | Threshold range (ppm) |
|---|---|---|---|---|
| Soil | Na | Herbaceous | $EC_{25}$ | 202–270 |
| Soil | Na | Woody | $EC_{25}$ | 67.5–300 |
| Root uptake | Na | All species | $EC_{25}$ | 67.5–300 |
| Water solution | Cl | Wetland | LOEL | 300– 1500 |
| Soil | Cl | Woody | $EC_{25}$ | 215–500 |
| Root uptake | Cl | All species | $EC_{25}$, LOEL | 215–1500 |
| Soil | NaCl | Woody | $EC_{25}$ | 600–5500 |
| Solution culture | NaCl | Herbaceous | $EC_{25}$ | <2500–10 000 |
| Solution culture | NaCl | Wetland | NOEL, LOEL | 280–66 600 |
| Solution culture | NaCl | Woody | $EC_{25}$, CTV | 836–25 000 |
| Root uptake | NaCl | All species | $EC_{25}$, CTV, NOEL, LOEL | 280–66 600 |

**Table 20: Range of threshold values estimated for herbaceous tissue concentrations following soil or water solution exposure**

| Pathway | Form | Plant form | Threshold type | Threshold range (ppm) |
|---|---|---|---|---|
| Soil | Na | Herbaceous | $EC_{25}$ | <280–17 800 |
| Soil | Cl | Herbaceous | $EC_{25}$ | <4100 |

**Table 21: Range of threshold values estimated for woody tissue concentrations following aerial exposure**

| Pathway | Form | Plant form | Threshold type | Threshold range (ppm) |
|---|---|---|---|---|
| Vegetation conc. | Na | Woody | $EC_{25}$ | 200–16 100 |
| | | | | |
| Vegetation conc. | Cl | Woody | $EC_{25}$, CTV | 800–70 700 |
| | | | | |
| Foliar spray conc. | NaCl | Woody | CTV | 7140 |

**Table 22: Calculation of the number of particles of salt that need to be ingested in order to reach critical toxicological values assuming a model 28 g House sparrow consuming particles at the upper end of its known preference range**

| Critical toxicological value (CTV) | Rationale | No. 2.4-mm diameter spherical salt particles to attain CTV in 28 g bird | No. 2.4-mm diameter cubic salt particles to attain CTV in 28 g bird |
|---|---|---|---|
| 266 mg/kg | Breach of homeostasis | 0.47 | 0.25 |
| 500 mg/kg | Oedematous lesions in the gizzard | 0.88 | 0.47 |
| 1500 mg/kg | Overt signs of toxicity. Mortality first recorded. | 2.6 | 1.4 |
| 3000 mg/kg | Approximate median lethal dose | 5.2 | 2.8 |

**Table 23: Calculation of the number of particles of salt that need to be ingested in order to reach critical toxicological values assuming a model 28 g House sparrow consuming particles of average size**

| Critical toxicological value (CTV) | Rationale | No. 0.5-mm diameter salt particles to attain CTV | | No. salt particles as proportion of average gizzard grit count (580 particles as in Gionfriddo and Best, 1995) | |
|---|---|---|---|---|---|
| | | Spherical particles | Cubic particles | Spherical particles | Cubic particles |
| 266 mg/kg | Breach of homeostasis | 52 | 27 | 9.0% | 4.7% |
| 500 mg/kg | Oedematous lesions in the gizzard | 98 | 51 | 17% | 8.8% |
| 1500 mg/kg | Overt signs of toxicity. Mortality first recorded. | 294 | 154 | 51% | 27% |
| 3000 mg/kg | Approximate median lethal dose | 587 | 307 | 101% | 53% |

**Table 24: Quotient calculation results for aquatic biota – Tier I**

| Group | Name | Application factor | Quotient |
|---|---|---|---|
| Microorganisms | *Pseudomonas putida* | 5 | $Quotient_{(e)}$ = 1 250<br>$Quotient_{(m)}$ =1 250 |
| Plants | *Scenedesmus quadricauda* | 5 | $Quotient_{(e)}$ = 40.3<br>$Quotient_{(m)}$ = 43.5 |
| Invertebrates | *Daphnia magna* | 10 | $Quotient_{(e)}$ = 30.12<br>$Quotient_{(m)}$ = 32.5 |
| Vertebrates | *Lepomis macrochirus* | 5 | $Quotient_{(e)}$ = 250<br>$Quotient_{(m)}$ = 270 |

(m) = Using measured water concentration; (e) = Using estimated water concentration

**Table 25: Summary of impact assessment for terrestrial biota – Tier I**

| Group | Name | Application factor | Quotient |
|---|---|---|---|
| Plants | *Raphanus sativa* | 10 | Quotient = 3.25 |
| Invertebrates | *Eisenia fetida* | 10 | Quotient = 1 |
| $Vertebrates_{(mammals)}$ | *Silivagus floridanus* | none | Quotient = 1 |
| $Vertebrates_{(birds)}$ | *Anas platyrhyncos* | 10 | Quotient = 1.22 |

**Table 26: Quotient calculation results for aquatic biota – Tier II**

| Group | Name | Application factor | Quotient |
|---|---|---|---|
| Microorganisms | *Pseudomonas putida* | none | $Quotient_{(e)}$ = 39<br>$Quotient_{(m)}$ = 41.5 |
| Plants | *Scenedesmus quadricauda* | none | $Quotient_{(e)}$ = 1.26<br>$Quotient_{(m)}$ = 1.3 |
| Invertebrates | *Daphnia magna* | 10 | $Quotient_{(e)}$ = 4.7<br>$Quotient_{(m)}$ = 5.0 |
| Vertebrates | *Lepomis macrochirus* | none | $Quotient_{(e)}$ = 7.8<br>$Quotient_{(m)}$ = 8.3 |

(m) = Using measured water concentration; (e) = Using estimated water concentration

**Table 27: Summary of Impact assessment for terrestrial biota – Tier II**

| Group | Name | Application factor | Quotient |
|---|---|---|---|
| Plants | *Raphanus sativa* | 5 | Quotient = 0.2 |
| Invertebrates | *Eisenia fetida* | 10 | Quotient = 0.15 |
| $Vertebrates_{(mammals)}$ | *Silivagus floridanus* | none | Quotient = 0.118 |
| $Vertebrates_{(birds)}$ | *Anas platyrhyncos* | 10 | Quotient = 0.126 |

**Figure 1:** Total 2-lane km of provincial saltable road

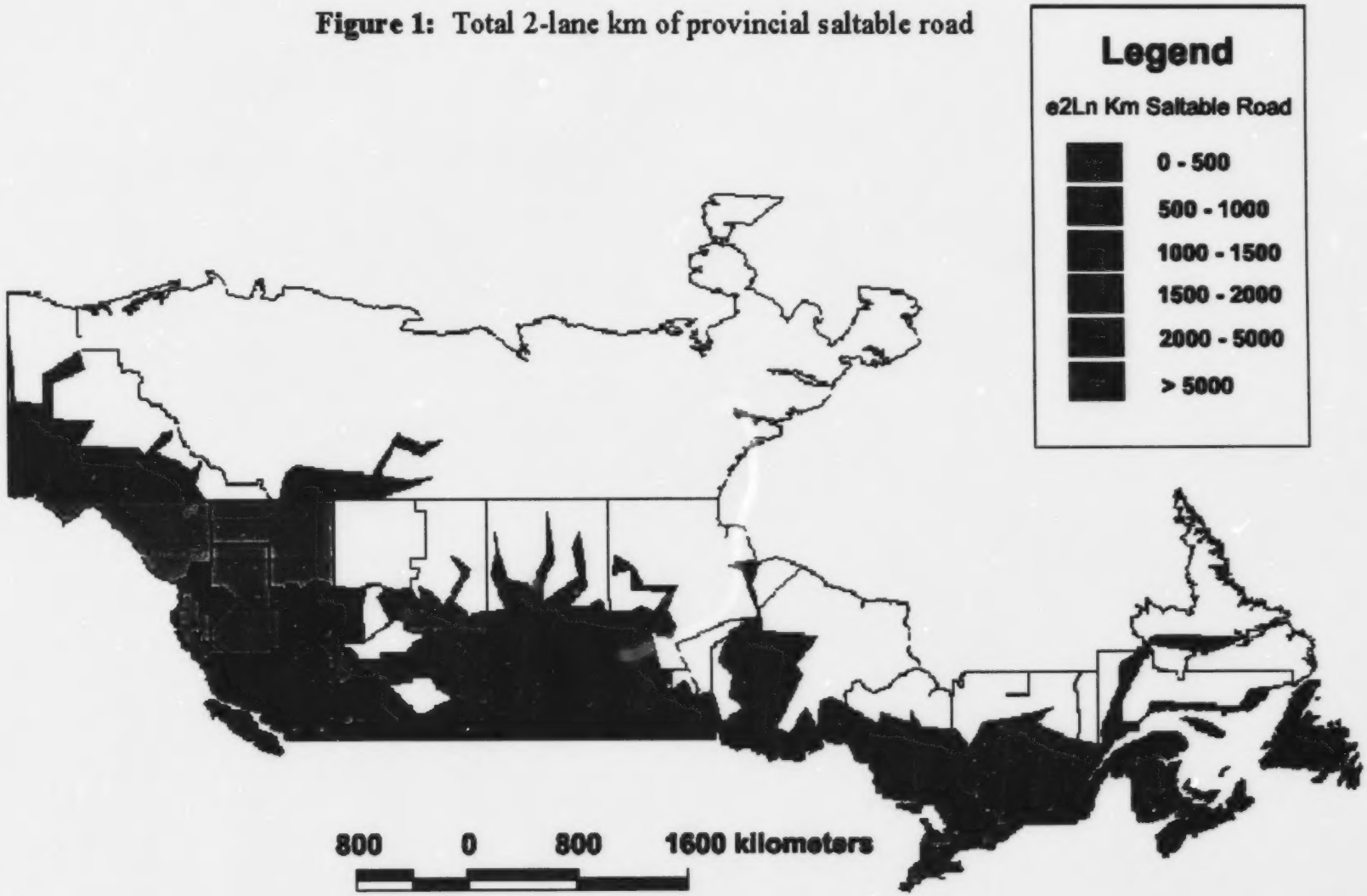


**Figure 2 :** Provincial road network area fraction
(sq. m saltable road / sq. m maintenance district)

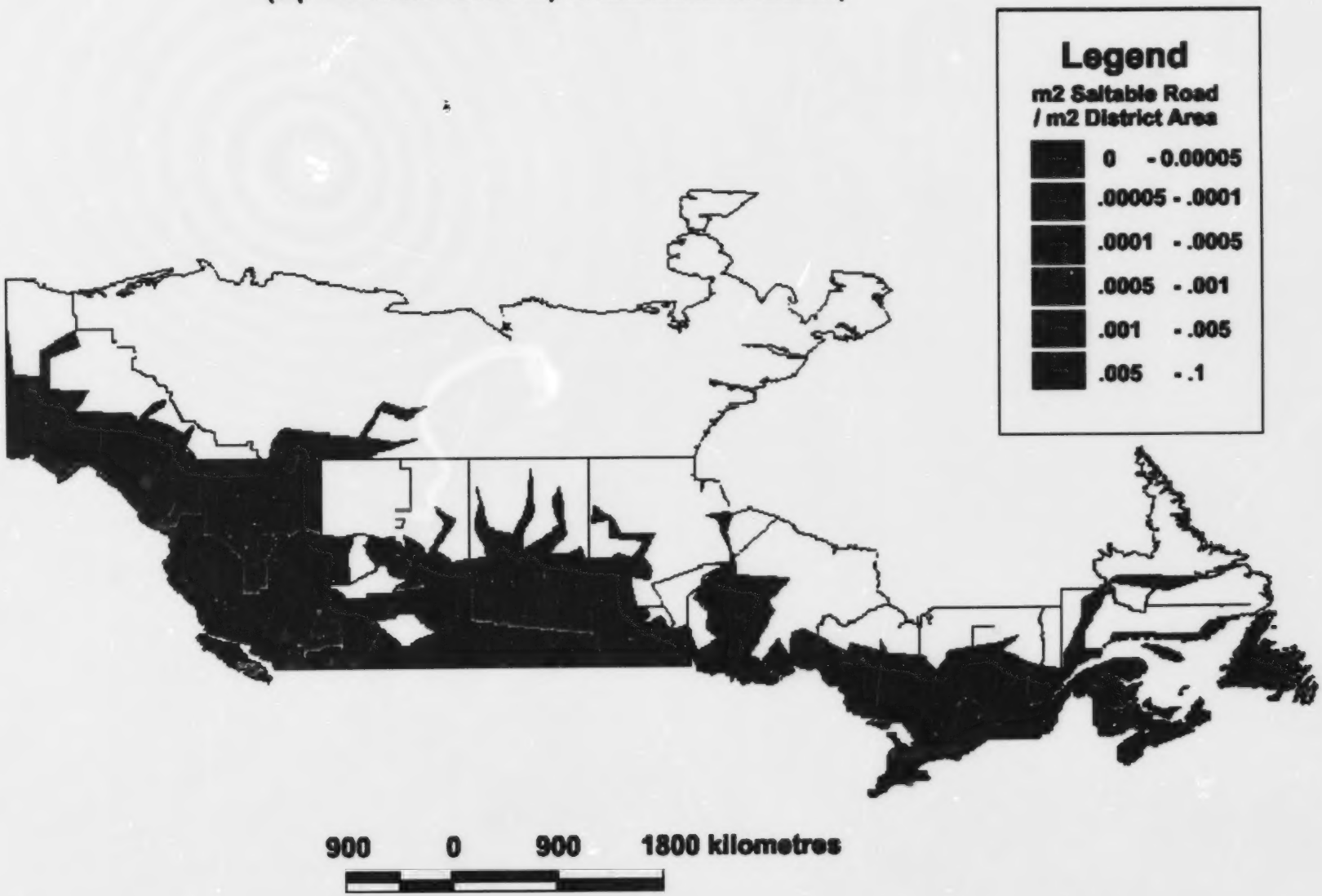


**Figure 3:** Sodium chloride road salt application rates by provincial agencies

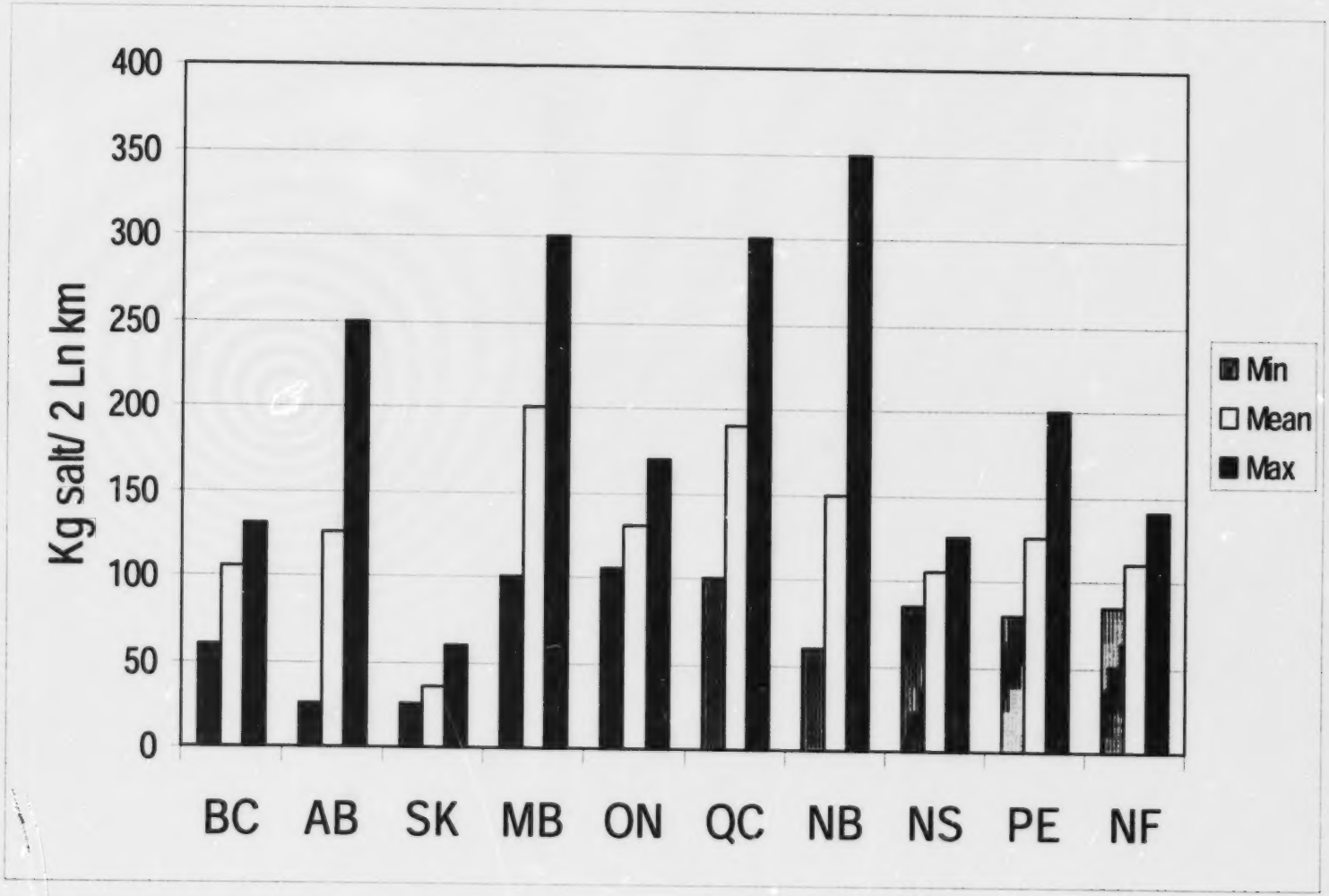


**Figure 4**: Average municipal application rates for sodium chloride road salts

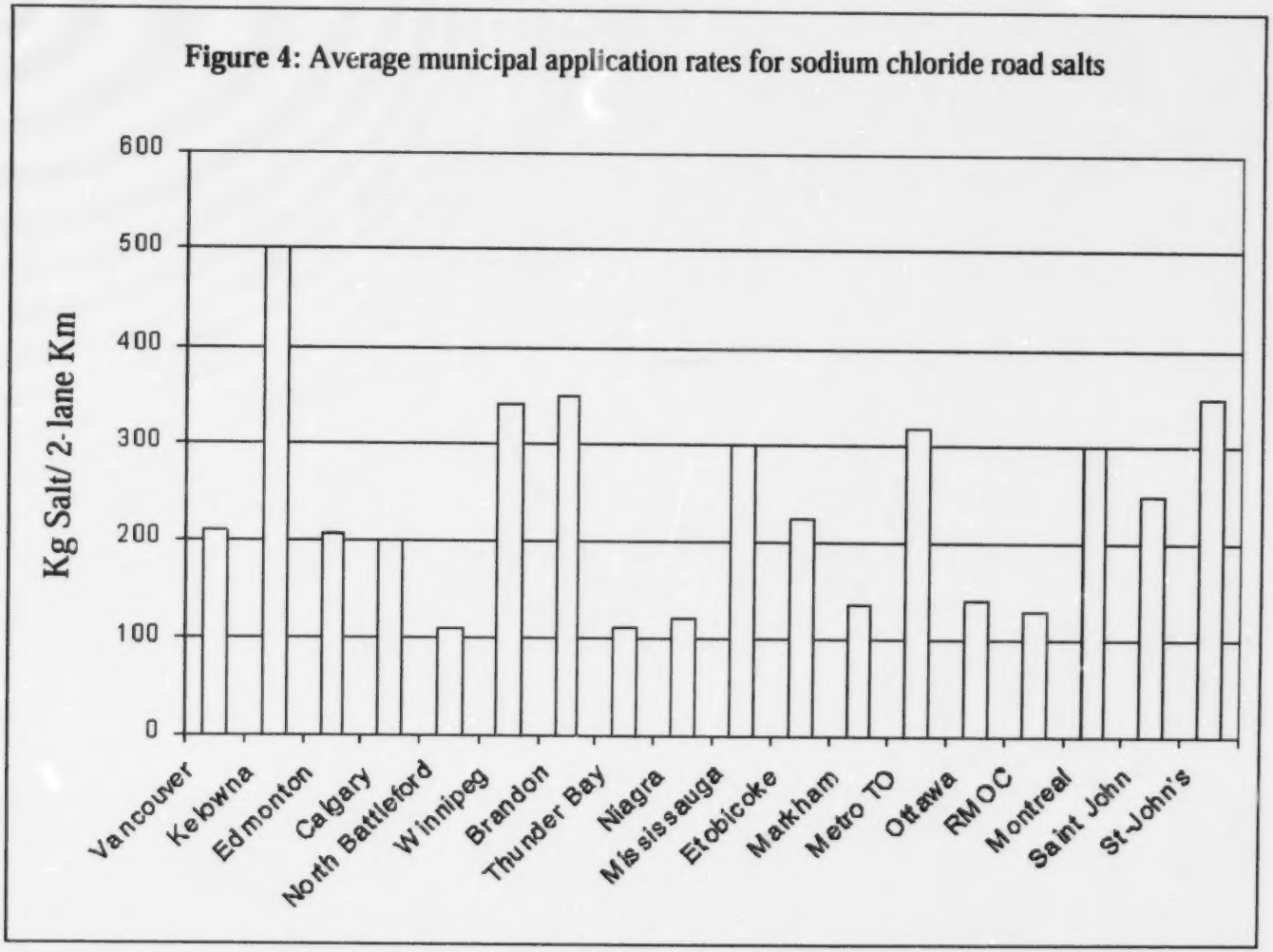


**Figure 5 :** Total tonnes of sodium chloride used by maintenance district

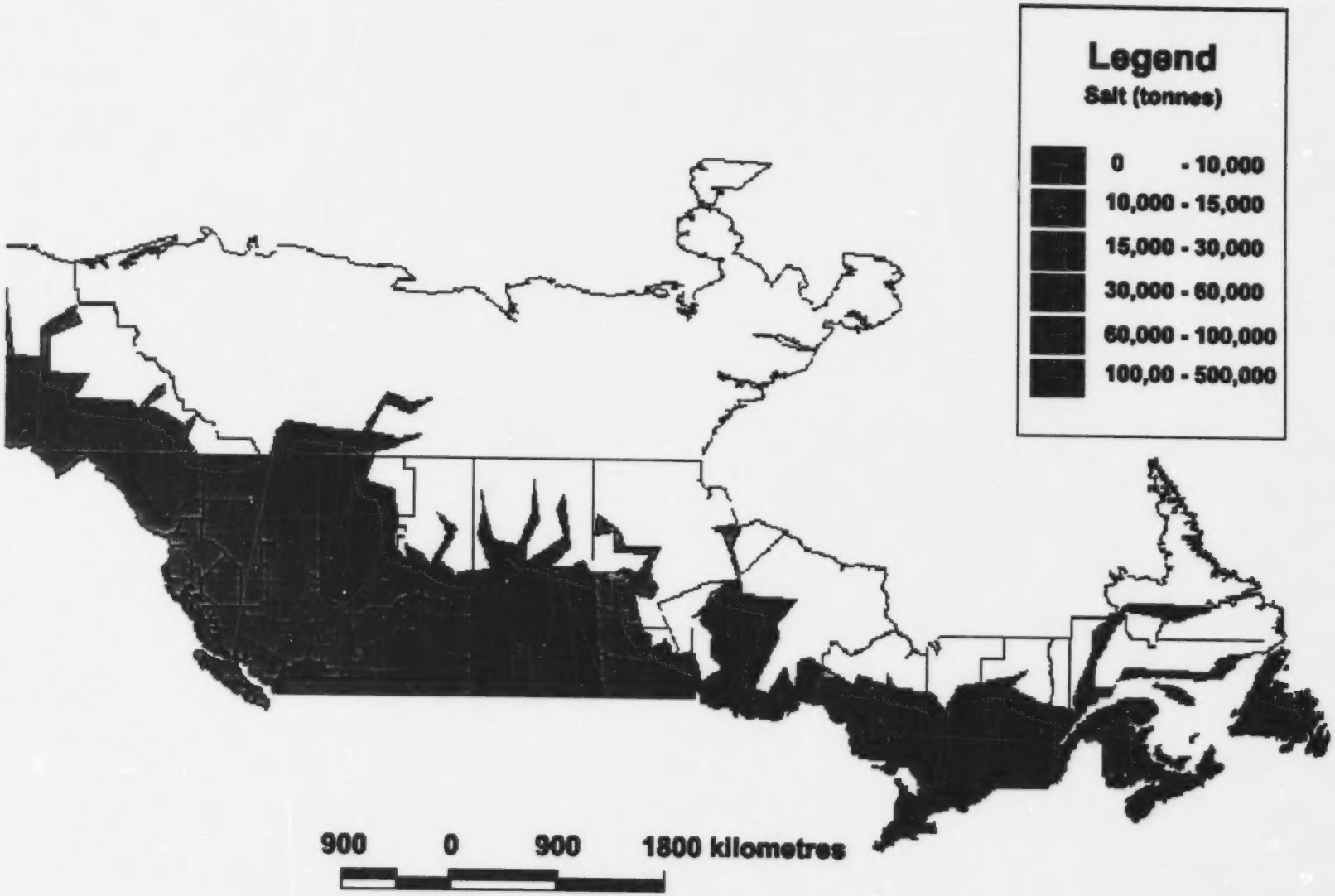


**Figure 6 :** Grams of salt per square meter of maintenance district

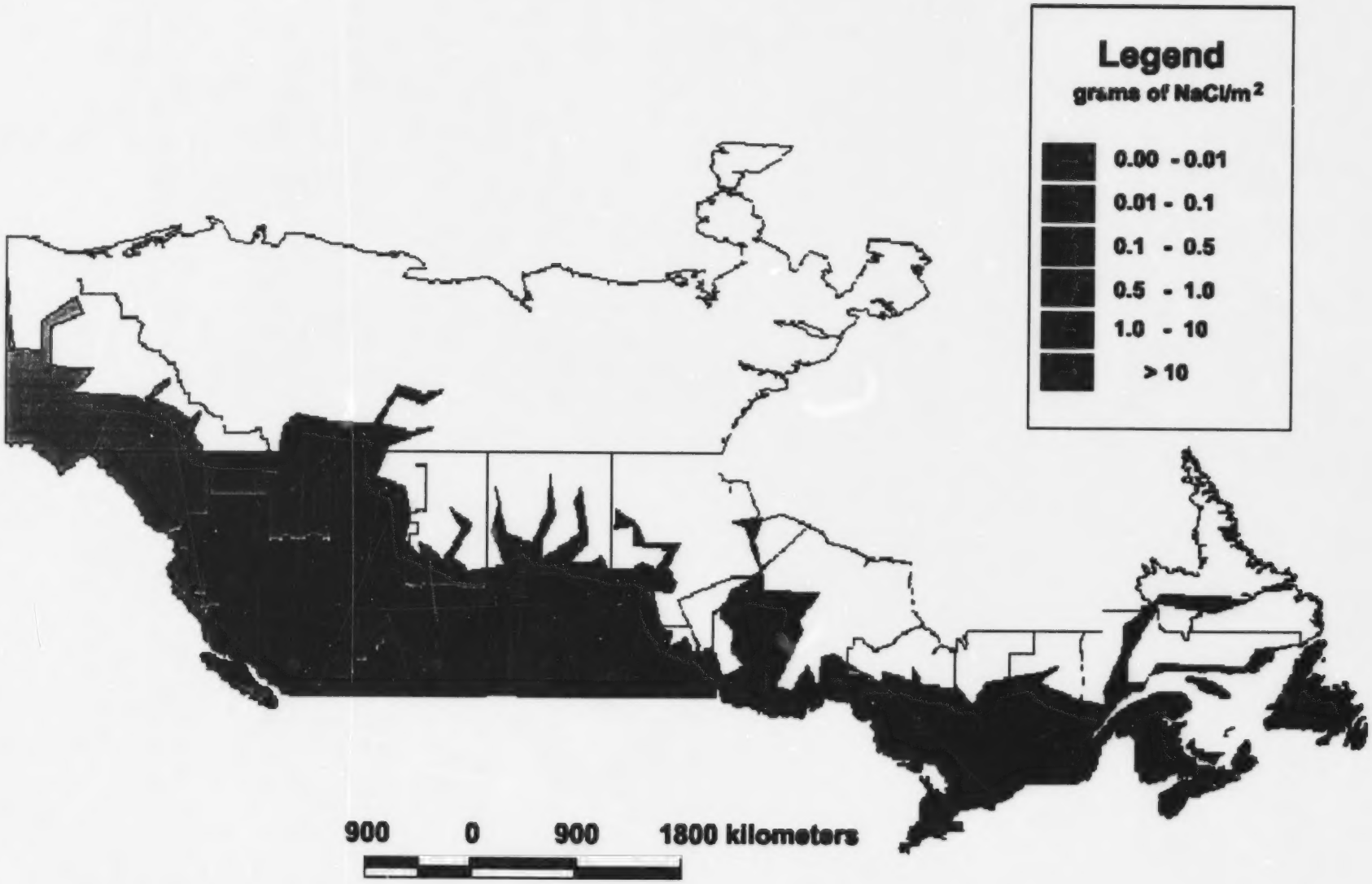
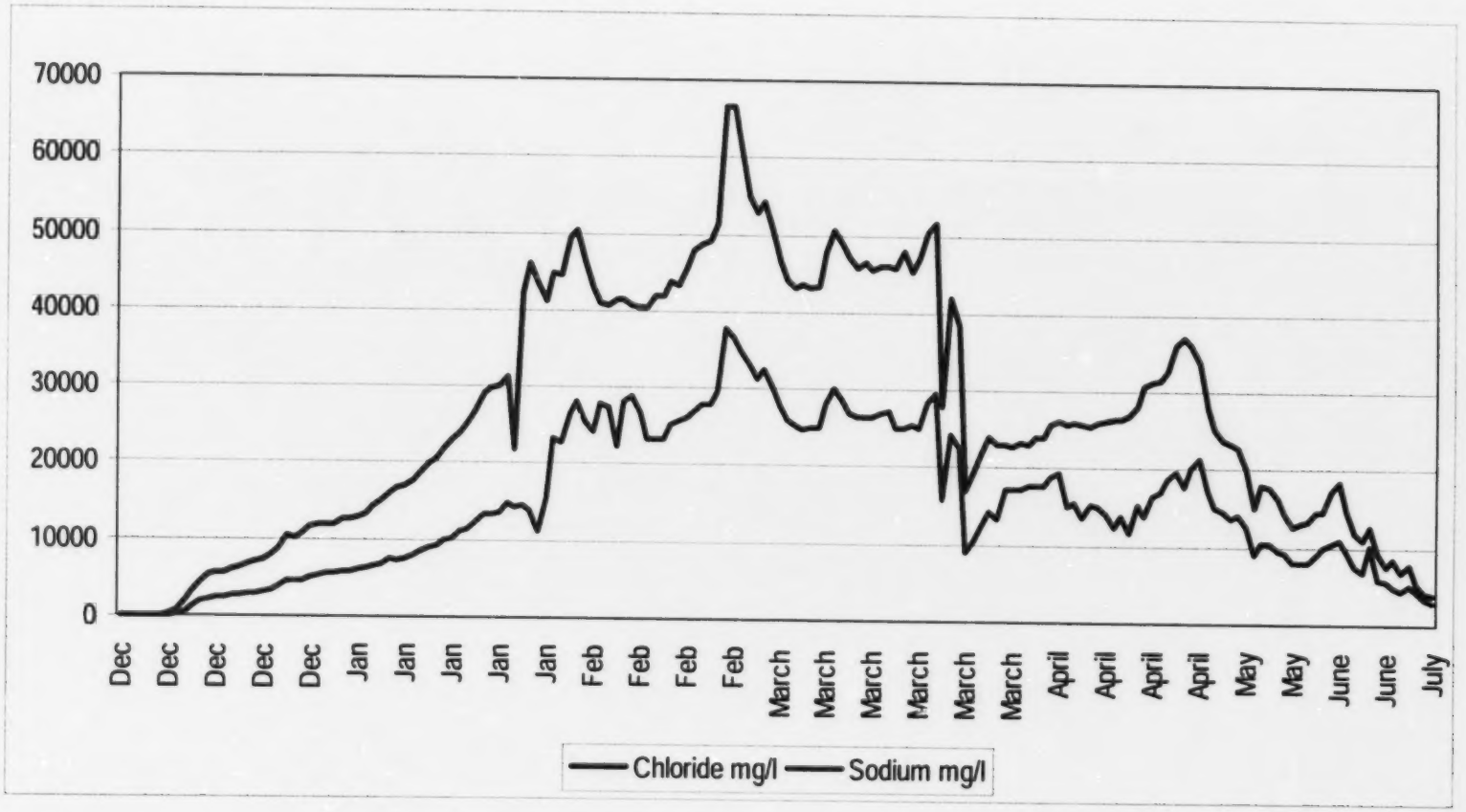
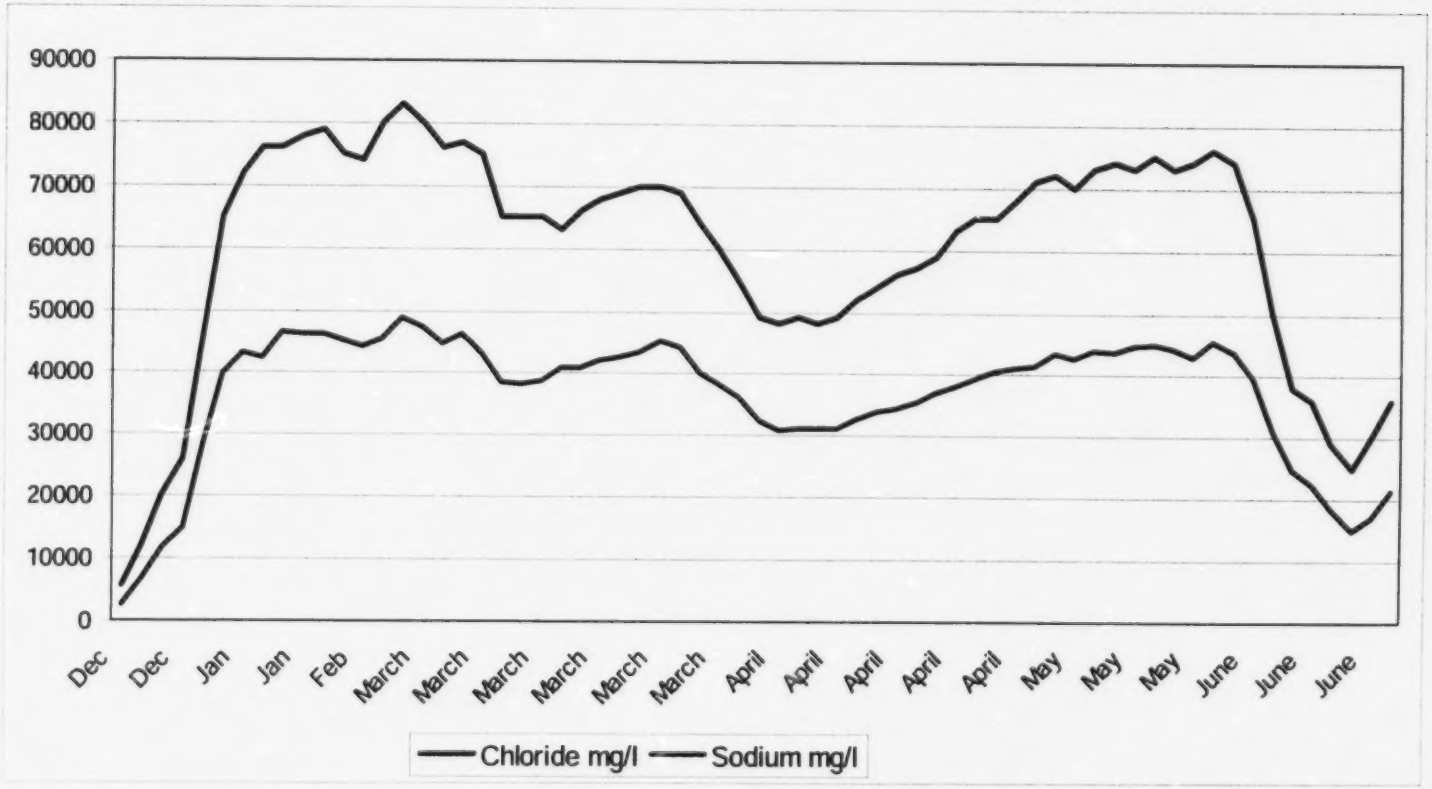


**Figure 7:** Average daily concentration of leachate from salt-treated sand pile 1975-76



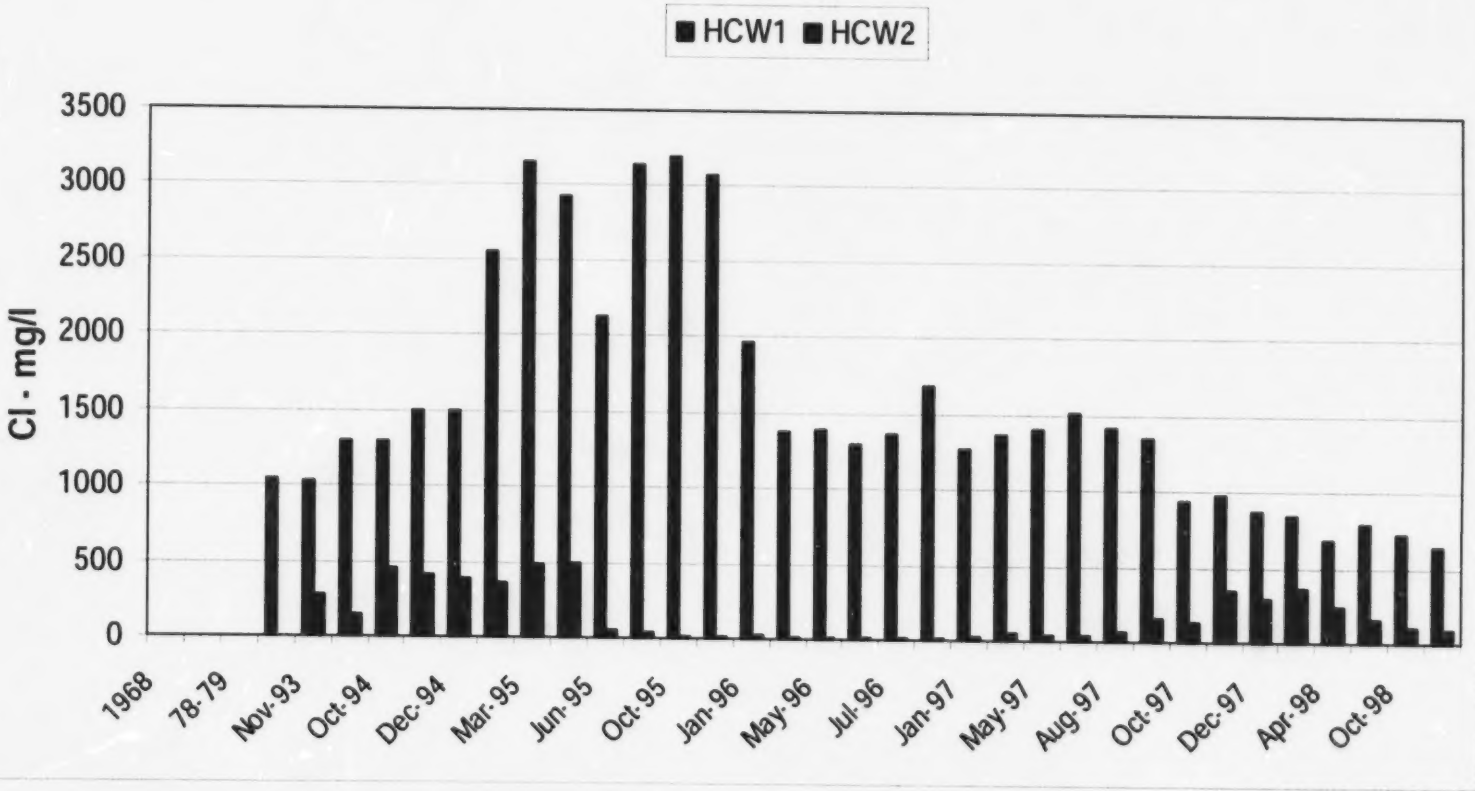

Source: NB DOE and DOT, 1978

**Figure 8:** Average daily concentration of leachate from salt-treated sand pile 1976-77




Source: NB DOE and DOT, 1978

**Figure 9:** Chloride concentrations in Heffley Creek municipal wells



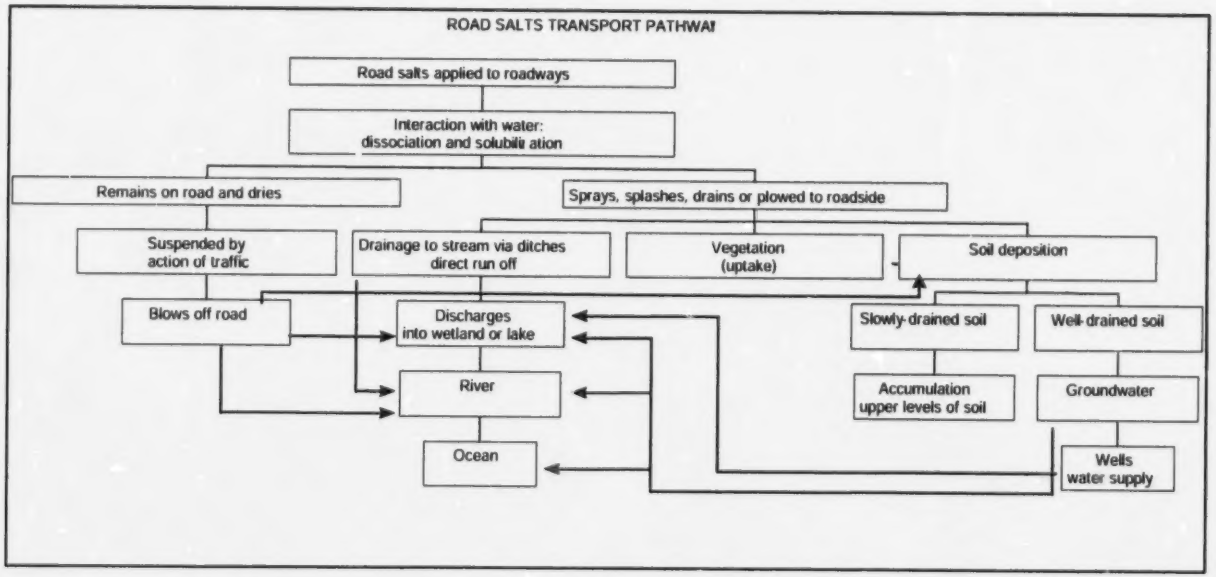



**Figure 10**: Road salts transport pathway

**Figure 11:** Runoff per unit area - based on midpoint values

**Figure 12:** Chloride loadings from road salts, g Cl/ $m^2$ watershed

**Figure 13:** Road salt chloride concentrations by watershed, based on midpoint runoff values

**Figure 14:** Observed chloride concentrations in Canadian watersheds

**Figure 15:** Portion of observed chloride concentrations derived from road salts (Cl concentration in runoff / concentration at stations), midpoint runoff values

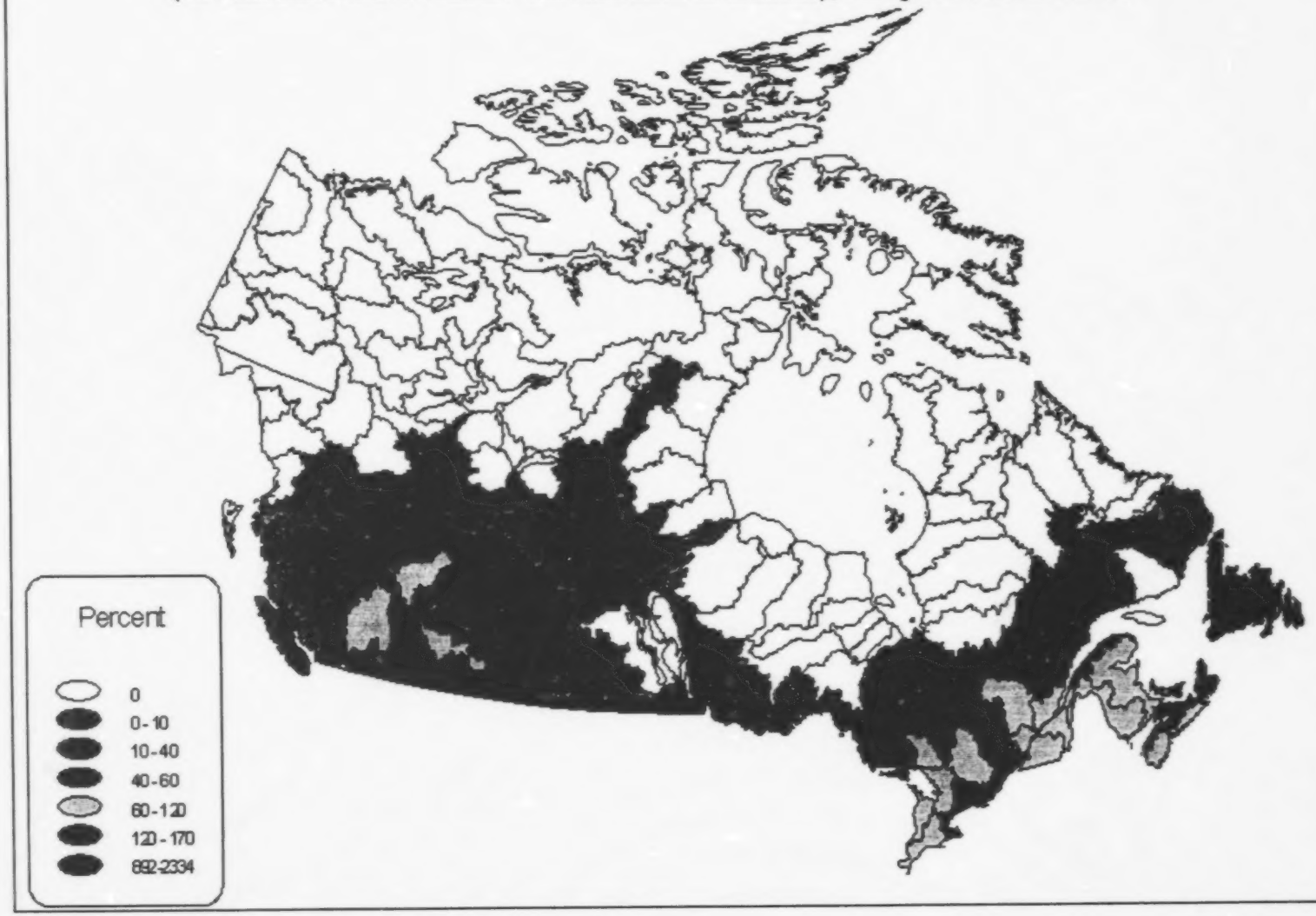


**Figure 14:** Observed chloride concentrations in Canadian watersheds

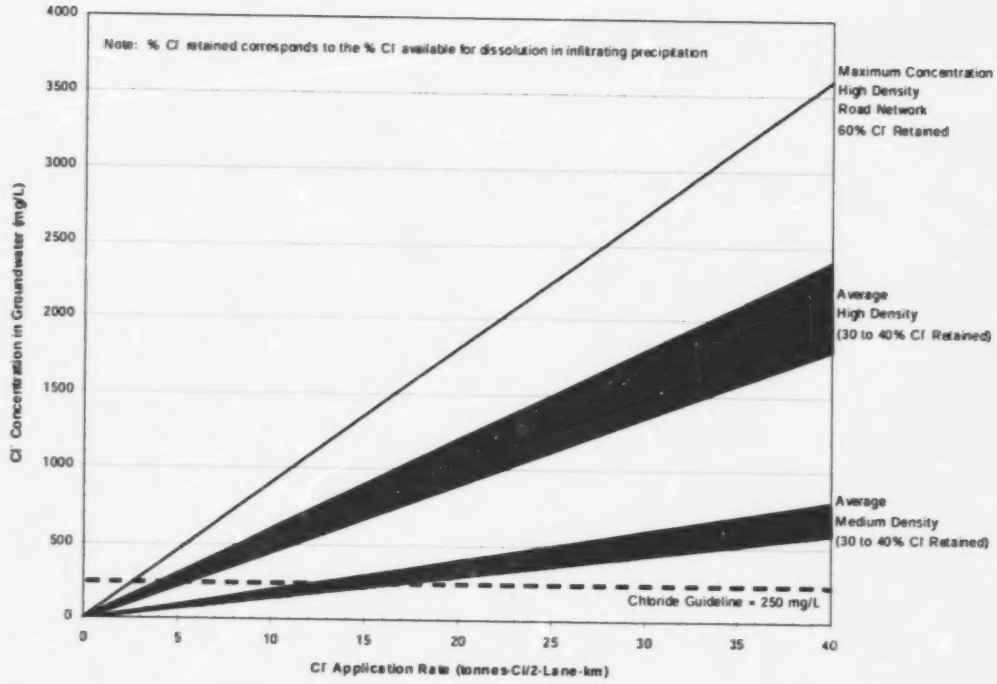



Figure 16: Estimated chloride concentrations in groundwater for various chloride application rates and a groundwater recharge rate of 10 cm/yr

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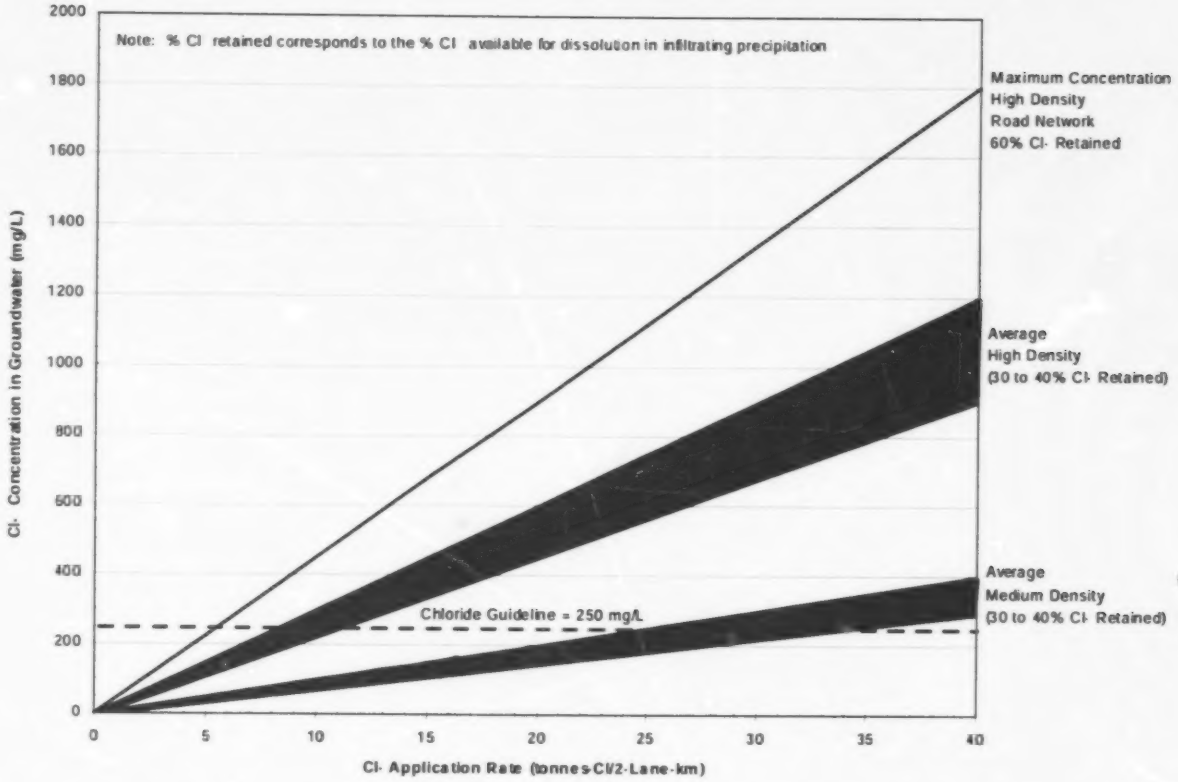


Figure 27 : Estimated chloride concentrations in groundwater for various chloride application rates and a groundwater recharge rate of 20 cm/yr

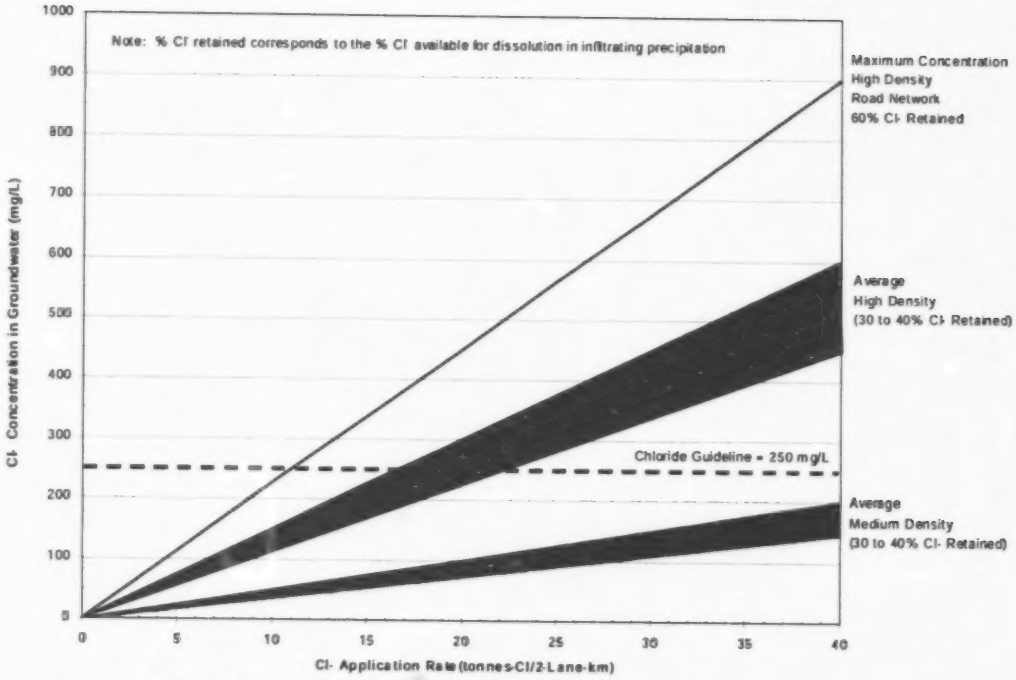


**Figure 18:** Estimated chloride concentrations in groundwater for various chloride application rates and a groundwater recharge range of 10 to 40 cm/yr.

Figure 28 : Estimated Cl- concentrations in groundwater for various Cl- application rates and a groundwater recharge rate of 40 cm/yr

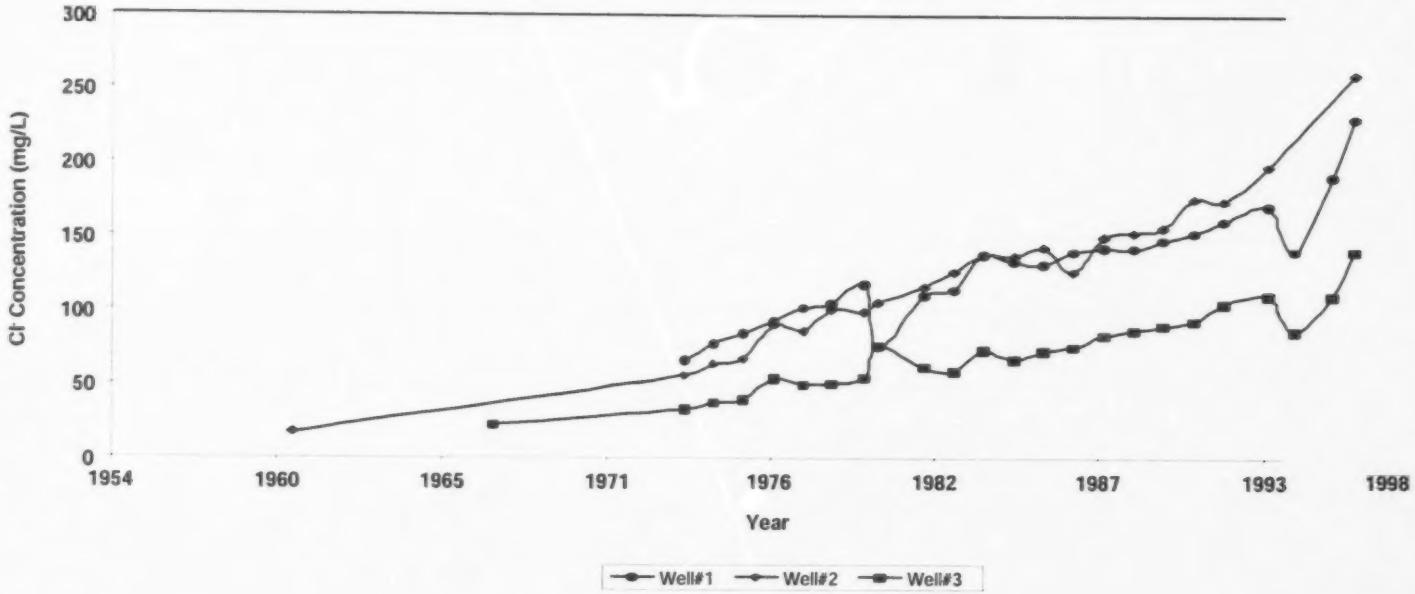


**Figure 19**: Chloride concentrations in groundwater from municipal production wells in southern Ontario

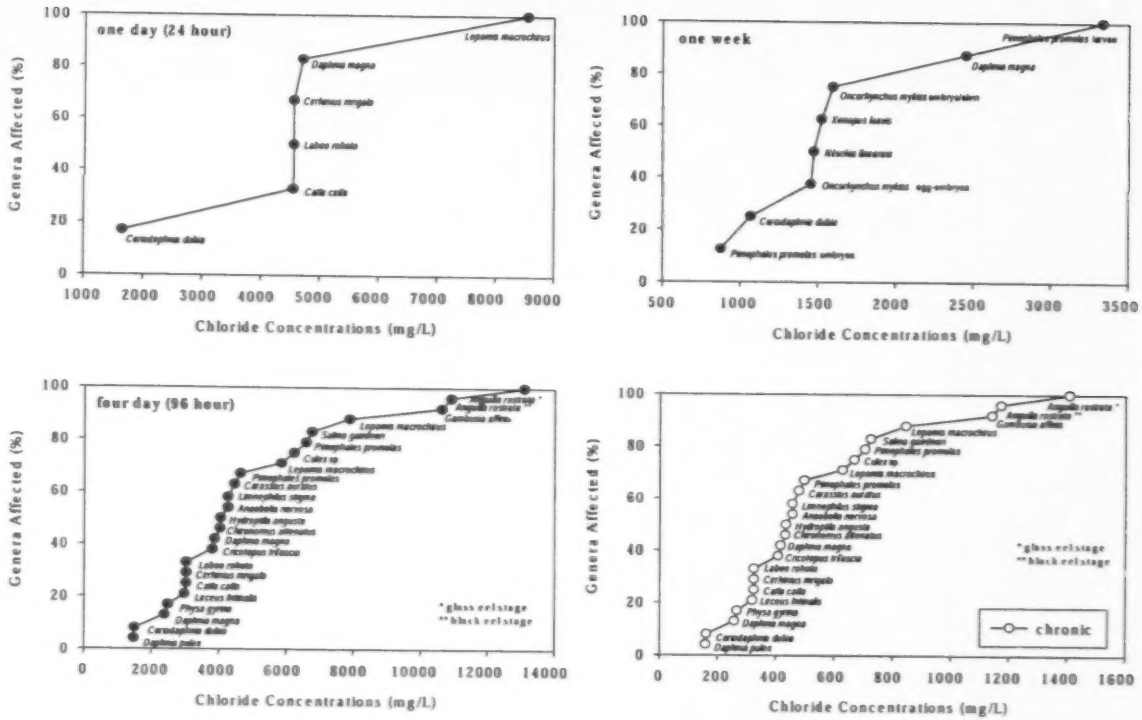


**Figure 20**: Experimental acute toxicity and predicted chronic toxicity for aquatic taxa

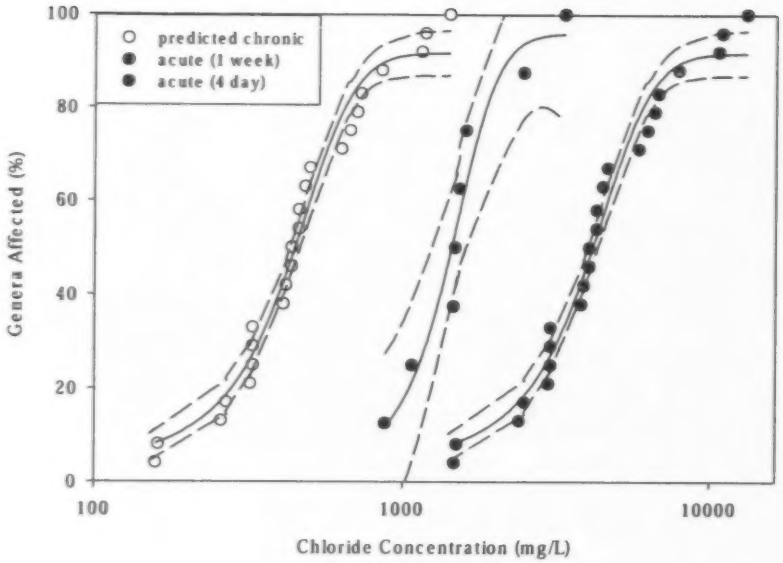


**Figure 21:** Experimental acute toxicity and predicted chronic toxicity for aquatic taxa

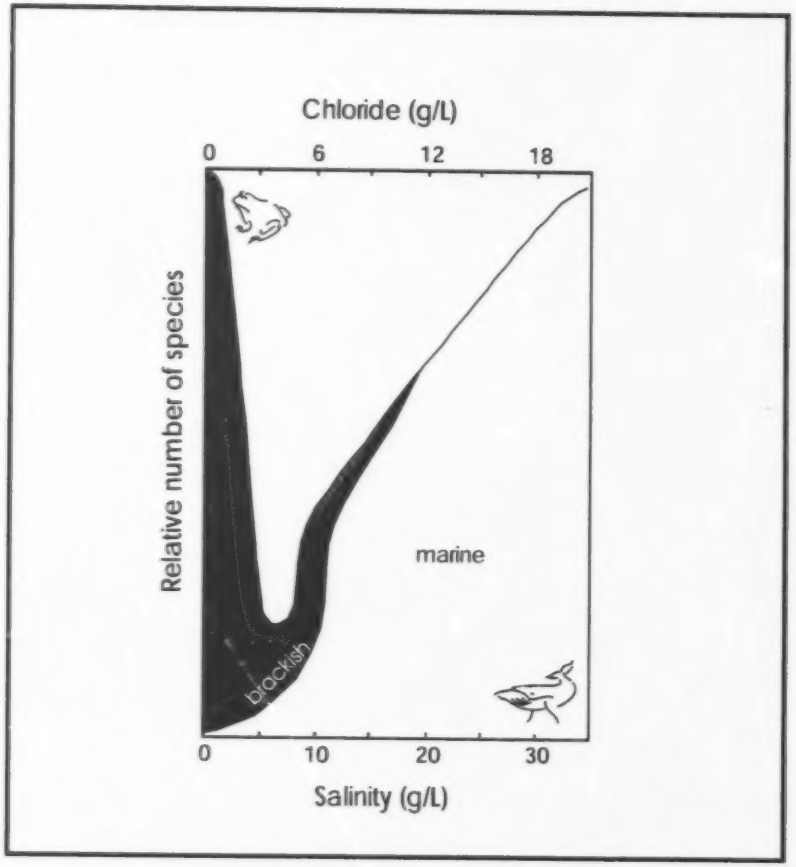


**Figure 22**: Species diversity across a salinity and chloride gradient

**Figure 23 : Index map to locate areas with low tomedium to high road salt application hazards, based on product of soil clay content with exchangeable sodium ratio**

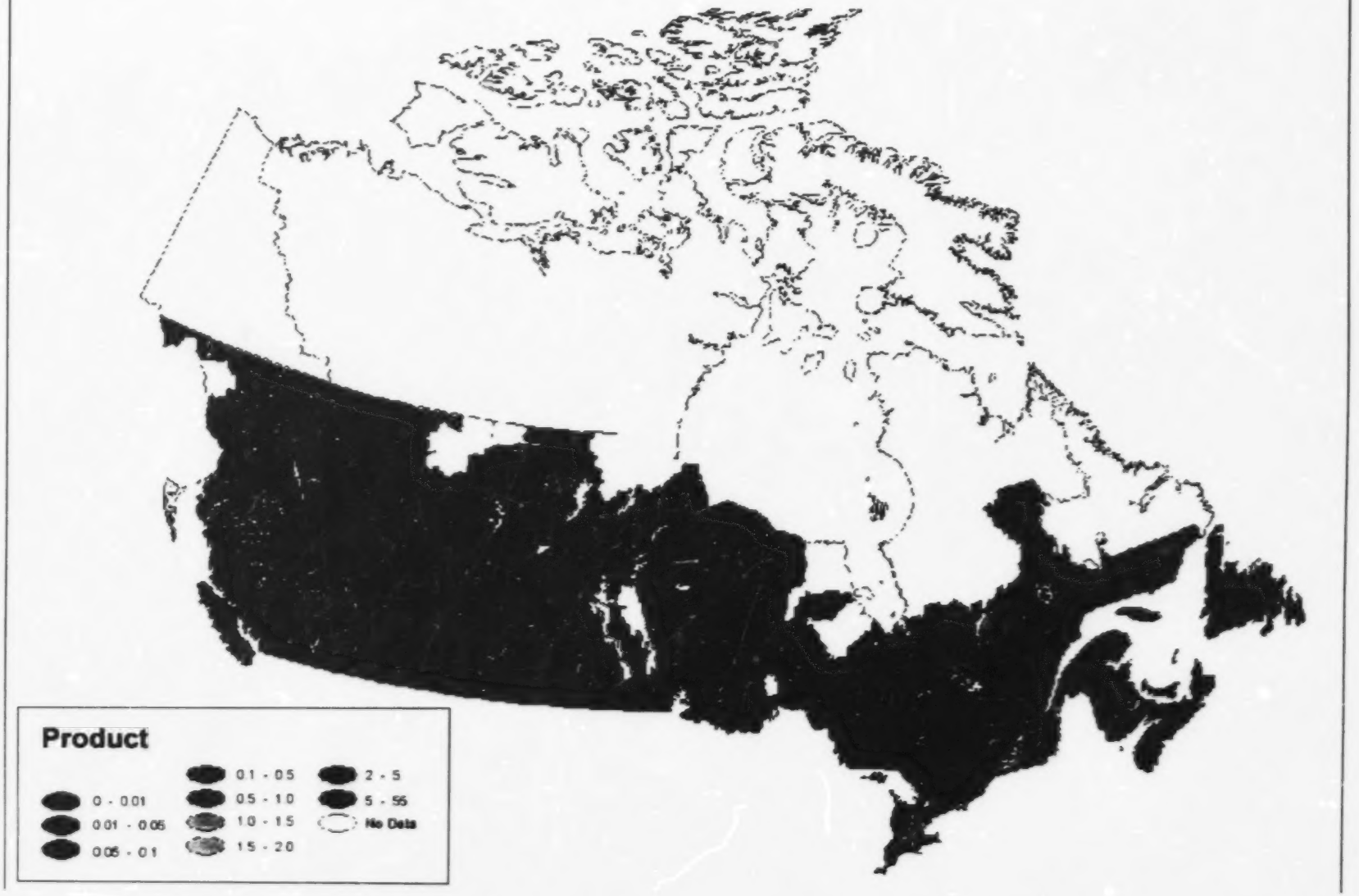

**Figure 24**: Estimates for total dissolved solids, electrical conductivity, and osmotic potential of average soil solution and surface waters, per Level 2 watersheds and per municipal boundaries, Central Canada

**Figure 25:** Estimates for total dissolved solids, electrical conductivity, and osmotic potential of average soil solution and surface waters, along roadsides per provincial road maintenance districts, Central Canada.

**Legend**

TDS (g / L)

| | |
|---|---|
| 0 | - 0.14 |
| 0.14 | - 1.0 |
| 1.0 | - 4.0 |
| 4.0 | - 8.0 |
| 8.0 | - 12.0 |
| 12.0 | - 16.0 |
| 16.0 | - 17.5 |

mS / cm

| | |
|---|---|
| 0 | - 0.22 |
| 0.22 | - 1.56 |
| 1.56 | - 6.25 |
| 6.25 | - 12.5 |
| 12.5 | - 18.75 |
| 18.75 | - 25.0 |
| 25.0 | - 27.35 |

osm, in atm

| | |
|---|---|
| -9.37 | - -8.56 |
| -8.56 | - -6.41 |
| -6.41 | - -4.27 |
| -4.27 | - -2.13 |
| -2.13 | - -0.53 |
| -0.53 | - -0.07 |
| -0.07 | - 0.0 |

**Figure 26: Exchangeable sodium percentage along roadsides per provincial road maintenance districts**

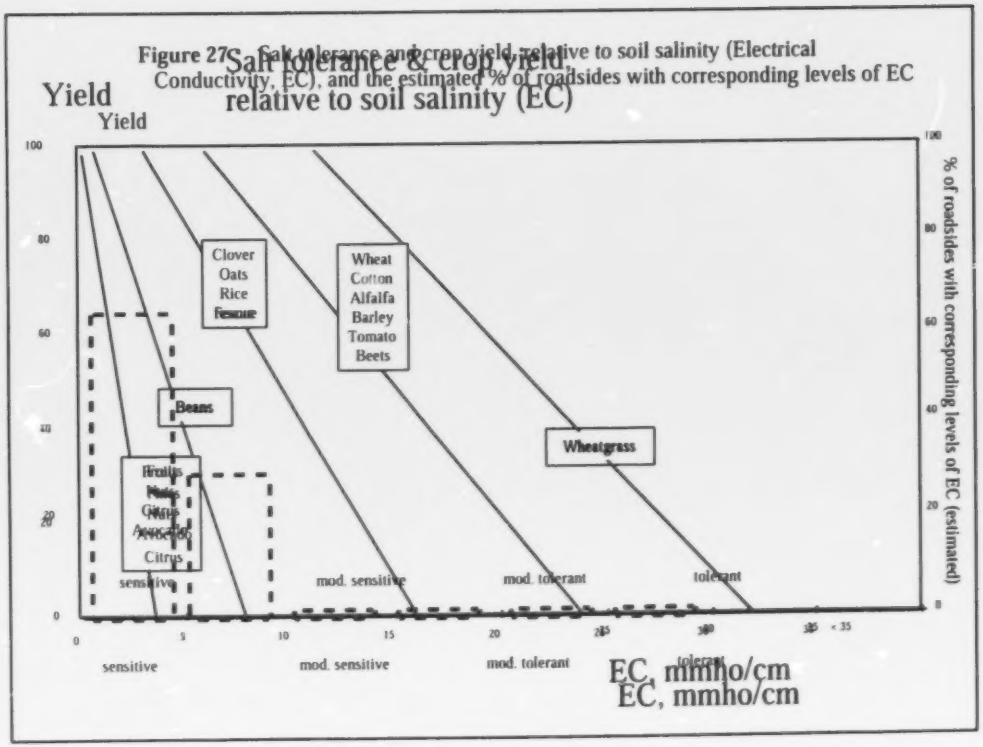


Figure 27. Salt tolerance and crop yield, relative to soil salinity (Electrical Conductivity, EC), and the estimated % of roadsides with corresponding levels of EC